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Date: 5 February 1968

RESEARCH PROJECT INITIATION

Project Title: Complex Metal Hydrides, High Energy Fuel Components for Solid Propellant Rocket Motors

Project No.: B-1520 (G-33-605)

Project Director: Dr. E. C. Ashby

Sponsor: Office of Naval Research, Department of the Navy

Agreement Period: From 1 March 1968 until 28 February 1969

Type Agreement: Contract No. N0001+-67-A-0159-0005

Amount: $28,550

Scientific Administrator

Power Branch
Material Sciences Division
Office of Naval Research
Department of the Navy
Washington, D. C. 20360

Reports Required

Progress - Semiannually, in quadruplicate
Technical - as may be required
Final Technical - upon completion of work.

Contract and Property Administrator

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Revised 30 Feb 68 B-1520

RA-3 (4/65)

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Date: June 4, 1975

Project Title: Complex Metal Hydrides, High Energy Fuel Components for Solid Propellant Rocket Motors

Project No: G-33-665 (formerly B-1520)

Principal Investigator: Dr. E. C. Ashby

Sponsor: Office of Naval Research; Arlington, VA 22217

Effective Termination Date: 12/31/74 (End performance period(*

Clearance of Accounting Charges: by 12/31/74

Grant/Contract Closeout Actions Remaining: Final Invoice & Closing Doc's.
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*Contract Mod. No. 11 deletes final report requirements (to be part of reporting under follow-on project G-33-667), thereby fixing the Contract Expiration date at 12/31/74 (end of performance period).

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RA-4 (5/70)

Annual Report

to the

Office of Naval Research

March 1, 1968 to February 28, 1969

Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors

from

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This Research was sponsored by the Office of Naval Research
under Contract No. N00014-67-A-0159-005 and
ONR Contract Authority No. NR 093-050/12-5-67...429.

CONCERNING THE REACTION OF LITHIUM ALUMINUM HYDRIDE WITH DIETHYLMAGNESIUM IN DIETHYL ETHER

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Abstract

The reaction of lithium aluminum hydride with diethylmagnesium in diethyl ether has been studied in detail. The reaction was found to proceed according to the following equations:

$$LiAlH_4 + 2(C_2H_5)_2Mg \rightarrow 2\ MgH_2 + LiAl(C_2H_5)_4$$

$$2\ LiAlH_4 + 3(C_2H_5)_2Mg \rightarrow 3\ MgH_2 + 2\ LiAl(C_2H_5)_3H$$

$$LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + LiAl(C_2H_5)_2H_2$$

$$2\ LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + 2\ LiAl(C_2H_5)H_3$$

The identity of the aluminum containing products was established by comparison with the authentic compounds prepared by the redistribution of $LiAlH_4$ and $LiAl(C_2H_5)_4$. Attempts to prepare C_2H_5MgH and $HMgAlH_4$ by the reaction of $LiAlH_4$ and $(C_2H_5)_2Mg$ are discussed.

Introduction

In a paper on the preparation of group II hydrides Schlesinger, et al.,[2] reported that magnesium hydride could be prepared from lithium aluminum hydride and diethylmagnesium in diethyl ether only under very special conditions. It was reported that lithium aluminum hydride in diethyl ether must be added slowly to a 0.5 M solution of diethylmagnesium in diethyl ether until the ratio of lithium aluminum hydride to diethylmagnesium is 0.3:1. It was emphasized that unless this procedure was followed exactly, either no magnesium hydride was formed, or if magnesium hydride were formed, it contained excessive aluminum. Under ideal conditions the magnesium hydride product contained 0.1 mole of aluminum per mole of magnesium. The Schlesinger group uncovered a further interesting aspect concerning this reaction. They found that if diethylmagnesium in diethyl ether was added to a large excess of lithium aluminum hydride solution, a clear solution resulted, from which a compound analyzing for $HMgAlH_4$ precipitated on addition of benzene. The precipitate was not further characterized. These workers further reported that when lithium aluminum hydride in diethyl ether was added to diethylmagnesium solution, a precipitate occurred, but on continued addition of lithium aluminum hydride solution, the precipitate redissolved. On long standing a gelatinous precipitate formed which analyzed similar to the above. In view of these interesting features, the report of the possible preparation of $HMgAlH_4$, and the fundamental nature of this reaction, a more detailed study seemed appropriate. It was our intention to study the reaction of lithium aluminum hydride with diethylmagnesium in diethyl ether solvent varying the mode of addition and stoichiometry of

the reaction in an attempt to describe the products of the reaction with stoichiometry. It was also of great interest to us to attempt to isolate and characterize two possible intermediates in this reaction, $HMgAlH_4$ and C_2H_5MgH.

Experimental

Apparatus - Reactions were performed under dry nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a manganese oxide recirculating system to remove oxygen. Infrared spectra were obtained on a Perkin Elmer 621 Spectrophotometer using either KBr or CsI liquid or mull cells. Infrared spectra of the solids were obtained in Nujol mulls.

Analytical - Total gas analysis was accomplished by hydrolysis of solid or solution samples and measuring the resultant liberated gas. No separation of gases was made although diethyl ether was trapped with a dry ice-acetone trap. Magnesium was determined by titration with EDTA at pH 11 using Eriochrome Black T as an indicator. When aluminum was present, it was masked by complexation with triethanolamine. Aluminum was determined by adding excess EDTA and back titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. Halide was determined by the Volhard procedure, and lithium by flame photometry.

Materials - All solvents were distilled immediately before use from lithium aluminum hydride or sodium aluminum hydride depending on the

boiling point of the solvent.

Diethylmagnesium ($(C_2H_5)_2Mg$) was prepared by the dioxane precipitation of $MgBr_2$ from ethylmagnesium bromide.[3] Triply sublimed magnesium was obtained from Dow Chemical Corporation and ethyl bromide from Fisher Scientific Company. Ethyl bromide was dried over anhydrous $MgSO_4$ and distilled prior to use. Ethylmagnesium bromide was prepared in diethyl ether in the usual manner. The $(C_2H_5)_2Mg$ solution was standardized by magnesium analysis. Bromide analysis was negative.

Lithium aluminum hydride ($LiAlH_4$) was obtained from Ventron, Metal Hydride Division. A solution was prepared by stirring a slurry of $LiAlH_4$ in diethyl ether overnight. The solution was filtered through a glass fritted funnel using dried Celite filter aid. The clear solution was standardized by aluminum analysis.

Lithium tetraethylalanate ($LiAl(C_2H_5)_4$) was prepared by a modification of the procedure of Zakharkin.[4] Lithium metal was obtained from Foote Minerals. A lithium dispersion was prepared by heating lithium metal in mineral oil to approximately 200° and stirring with a high speed stirrer in a creased flask. The mineral oil was removed from the dispersion by washing with benzene. The dispersion was allowed to react with triethylaluminum (obtained from Texas Alkyls) at the temperature of refluxing benzene. After allowing the reaction mixture to reflux for 2 hours the solution was filtered, and the product crystallized from the filtrate on cooling. The $LiAl(C_2H_5)_4$ was recrystallized from a benzene-hexane mixture. After drying <u>in vacuo</u> diethyl ether was distilled onto the solid, and the solution standardized by aluminum analysis. Infrared spectra of the solid and solution agreed with the reported spectra.[5]

Infrared Study of the Reaction of $LiAlH_4$ with $(C_2H_5)_2Mg$ in Diethyl Ether - A 0.10 M solution of $(C_2H_5)_2Mg$ in diethyl ether was placed in a 3-neck round bottom flask fitted with a condensor, an addition funnel, and a 3-way stopcock to enable samples to be removed by syringe for infrared analysis. A 1.32 M solution of $LiAlH_4$ was placed in the addition funnel. Increments of the $LiAlH_4$ solution were added to the magnetically stirred $(C_2H_5)_2Mg$ solution. After each addition the solution was stirred for 15 minutes. Then the stirring was stopped to allow the precipitate to settle. A sample of the supernatant was withdrawn by syringe under nitrogen for infrared analysis. The addition was continued until $LiAlH_4$ was in large excess. The entire experiment was repeated using a 0.582 M $(C_2H_5)_2Mg$ solution. In a like manner a 0.883 M solution of $(C_2H_5)_2Mg$ in diethyl ether was added in increments to solutions of $LiAlH_4$ of the following concentrations: 0.100, 0.500, and 1.00 M. In Figure 1 a typical set of infrared spectra is shown.

Redistribution of $LiAlH_4$ and $LiAl(C_2H_5)_4$ - Reaction between $LiAlH_4$ and $LiAl(C_2H_5)_4$ was performed by mixing the reactants in appropriate ratio from standard solutions. After thoroughly mixing the solutions, infrared spectra were obtained.

Preparation of MgH_2 from $(C_2H_5)_2Mg$ and $LiAlH_4$ - A reaction, using the exact conditions reported by Schlesinger, et al., was carried out. A diethyl ether solution of $LiAlH_4$ (1.24 M) was added slowly from an addition funnel to a 0.5 M solution of $(C_2H_5)_2Mg$. The ratio of reactants was 0.3 $LiAlH_4$:1 $(C_2H_5)_2Mg$. An immediate precipitate formed. After stirring for one hour at room temperature, the solution was filtered. The precipitate was washed with ether and dried for one hour in vacuo at 70-80°C.

The precipitate analyzed as $Al_{0.093}MgH_{1.85}$. The infrared spectrum of the solid product showed a very broad band from 950-1450 cm^{-1}.[6]

Another experiment using a 1.07 M solution of $(C_2H_5)_2Mg$ and a 1.54 M solution of $LiAlH_4$ was carried out in the same manner as above except that the reaction time was extended from one hour to 3 days. Analysis of the magnesium hydride gave: 6.26% H, 0% Al, 77.7% Mg, 16% $(C_2H_5)_2O$ by difference. The ratio of Mg:H is 1.00:1.94. The amount of MgH_2 recovered was 93% of the theoretical based on $LiAlH_4$ as the limiting reagent.

A reaction using 1.75 M $(C_2H_5)_2Mg$ and 1.54 M $LiAlH_4$ in diethyl ether in the same ratio as above after 5 days reaction gave magnesium hydride of the following analysis: 2.81% H, 6.70% Al, 26.42% Mg. The Al:Mg:H ratio was 0.228:1.00:2.57.

Reaction of $(C_2H_5)_2Mg$ with $LiAlH_4$ at Various Ratios - Lithium aluminum hydride and diethylmagnesium in diethyl ether were allowed to react at the following ratios of $LiAlH_4$:$(C_2H_5)_2Mg$ - 0.5:1, 0.67:1, 1:1, and 2:1. Each reaction was performed by adding the appropriate amount of 1.5 M ether solution of $LiAlH_4$ to 1.0 M ether solution of $(C_2H_5)_2Mg$. During the addition mild refluxing of the solvent took place due to the exothermic nature of the reaction. After stirring for one hour at room temperature, the solutions were filtered. The precipitates were washed with ether and dried *in vacuo* at 70-80° for one hour. Benzene was added to the filtrate, and the ether evaporated in order to crystallize the aluminum by-product. The amount of magnesium hydride recovered was always greater than 90% of the theoretical based on $(C_2H_5)_2Mg$. The reactions were repeated allowing a 3 day reaction time. Analyses of the precipitated magnesium hydride and the aluminum by-product compounds

obtained from solution are given in Table I.

Table 1. Elemental Analyses of the products from $LiAlH_4$:$(C_2H_5)_2Mg$ Reactions.

Reaction Ratio $LiAlH_4$:$(C_2H_5)_2Mg$	Precipitate Mg:H:Al:Li:$(C_2H_5)_2O$[c]	Product crystallized from the Filtrate - Li:Al:H:C_2H_5:$(C_2H_5)_2O$
0.50:1.0[a]	1:2.32:0.210:0.250:0.670	
0.67:1.0[a]	1:2.34:0.087:0.136:0.142	
0.67:1.0[b]	1:2.04:0.049:0.098:0.144	
1.0 :1.0[a]	1:2.36:0.177:0.145:0.098	
1.0 :1.0[b]	1:2.19:0.078:0.103:0.066	
2.0 :1.0[a]	1:3.00:0.350:0.350:0.250	
2.0 :1.0[b]	1:2.93:0.279:0.279:0.178	

[a]Reaction time was 1 hr. [b]Reaction time was 3 days. [c]$(C_2H_5)_2O$ determined by difference.

Attempt to Prepare C_2H_5MgH - A 0.12 M diethyl ether solution of $LiAlH_4$ was added very slowly to a 0.873 M ether solution of $(C_2H_5)_2Mg$. The ratio of $LiAlH_4$ to $(C_2H_5)_2Mg$ was 0.25:1. An infrared spectrum of the supernatant liquid taken after the precipitate had settled contained a band at 512 cm^{-1} [7] which is unshifted from the starting solution of $(C_2H_5)_2Mg$ in diethyl ether although the band is reduced in intensity. An infrared spectrum and analysis showed that the precipitate was MgH_2 (5.73% H, 0% Al, 73.64% Mg; Mg:H = 1:1.88). Analysis of the filtrate showed that 45% of the original magnesium was still in solution.

In another experiment a slurry of MgH_2 was stirred with a large excess of $(C_2H_5)_2Mg$ in diethyl ether overnight. Infrared analysis of the supernatant using a compensating cell with diethyl ether to blank out the solvent bands showed no bands other than those of $(C_2H_5)_2Mg$.

Reaction of MgH_2 with $LiAlH_4$ and $LiAl(C_2H_5)_4$ - A slurry of MgH_2 (0.004 Al:1 Mg) was stirred overnight with an ether solution of $LiAlH_4$. The solution was filtered and the precipitate washed thoroughly with diethyl ether. Analysis of the precipitate showed an Al:Mg ratio of 0.070:1.00.

An identical experiment was carried out using MgH_2 of the same analysis as above and a diethyl ether solution of $LiAl(C_2H_5)_4$. Analysis of the precipitate showed an Al:Mg ratio of 0.074:1.

Results and Discussion

In our study of the reaction of $LiAlH_4$ and diethyl magnesium in diethyl ether no clear solutions or precipitation and dissolution phenomena as reported by Schlesinger, et al.,[2] were observed. The mode of addition was found to be immaterial. The reaction was found to proceed in a stepwise manner exchanging the hydrogens of the $LiAlH_4$ with the ethyl groups of $(C_2H_5)_2Mg$ until all four hydrogens had been replaced as illustrated by equations 1-4.

$$LiAlH_4 + 2(C_2H_5)_2Mg \rightarrow 2\ MgH_2 + LiAl(C_2H_5)_4 \quad (1)$$

$$2\ LiAlH_4 + 3(C_2H_5)_2Mg \rightarrow 3\ MgH_2 + 2\ LiAl(C_2H_5)_3H \quad (2)$$

$$LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + LiAl(C_2H_5)_2H_2 \quad (3)$$

$$2\ LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + 2\ LiAl(C_2H_5)H_3 \quad (4)$$

In Figure 1 the infrared spectra of the supernatant solutions from a typical series of reactions are shown. At a ratio of $LiAlH_4$:$(C_2H_5)_2Mg$ of

0.5:1 (Eq. 1) the infrared spectrum shows no absorption in the Al-H stretching region (1600-1800 cm^{-1}) indicating the absence of any Al-H compounds. There is also a band present at 600-630 cm^{-1} which is characteristic of $LiAl(C_2H_5)_4$.[5] At this ratio the precipitate is MgH_2 containing some small aluminum impurity as shown by elemental analysis and infrared spectra. Magnesium hydride (Nujol mull) has a broad band in the infrared region, 950-1450 cm^{-1}, which is characteristic of the polymeric structure of MgH_2.[6] Only a slight trace of magnesium remains in the filtrate at this ratio. The absence of Al-H and magnesium from the filtrate prove that complete alkylhydrogen exchange has taken place at a 0.5:1 ratio of reactants. The addition of more $LiAlH_4$ simply results in a redistribution of the $LiAlH_4$ with the $LiAl(C_2H_5)_4$ to form the $LiAlH_n(C_2H_5)_{4-n}$ compounds (Eqs. 2-4).

In order to identify the $LiAlH_n(C_2H_5)_{4-n}$ compounds produced in these reactions, the compounds were prepared by an independent synthesis for spectral comparison. In this connection lithium tetraethylalanate [$LiAl(C_2H_5)_4$] was prepared from a lithium dispersion and triethylaluminum.

$$3\ Li + 4(C_2H_5)_3Al \rightarrow 3\ LiAl(C_2H_5)_4 + 4Al \qquad (5)$$

The resulting $LiAl(C_2H_5)_4$ was allowed to redistribute with $LiAlH_4$ in diethyl ether according to the following stoichiometry.

$$LiAlH_4 + 3\ LiAl(C_2H_5)_4 \rightarrow 4\ LiAl(C_2H_5)_3H \qquad (6)$$

$$LiAlH_4 + LiAl(C_2H_5)_4 \rightarrow 2\ LiAl(C_2H_5)_2H_2 \qquad (7)$$

$$3\ LiAlH_4 + LiAl(C_2H_5)_4 \rightarrow 4\ LiAl(C_2H_5)H_3 \qquad (8)$$

Infrared spectra of the resulting solutions are identical with those shown in Figure I, thus establishing the identity of the products produced in reactions 1-4.

The infrared spectra shown in Figure 1 indicate that the expected aluminum compounds have distinct spectra for reactions of $LiAlH_4$:$(C_2H_5)_2Mg$ in 0.5:1, 0.67:1, and 1:1 ratio (Eqs. 1-3). The product from the reaction at 2:1 ratio (Eq. 4) has a less distinct spectra. The position of all of the bands in these spectra are unshifted with variation in concentration of reactants or mode of addition.

In order to show that the infrared spectra in Figure 1 correspond to the actual compounds suggested, reactions were performed at the ratios shown in equations 1-4. The lithium hydridoalkylalanates were crystallized from the filtrate by adding benzene and evaporating the ether solvent. Analyses have not been carried out on these compounds as yet. However, there seems to be little doubt of their identity, since the $NaAlH_4$:$NaAl(C_2H_5)_4$ system has been shown to redistribute[8] to the expected $NaAlH_n(C_2H_5)_{4-n}$ compounds. In that study no evidence was found for the compound, $NaAl(C_2H_5)H_3$. The corresponding lithium compound is being studied very carefully by fractional crystallization to determine if it is a mixture of $LiAlH_2(C_2H_5)_2$ and $LiAlH_4$. As Figure 1 shows, the infrared is inconclusive on this point.

Contrary to the Schlesinger report, either mode of addition, ($LiAlH_4$ added to $(C_2H_5)_2Mg$ or $(C_2H_5)_2Mg$ added to $LiAlH_4$) causes an immediate precipitate to appear. The precipitate is a finely dispersed material that settles rapidly on standing except at a ratio of $LiAlH_4$:$(C_2H_5)_2Mg$ of 0.5:1. At this ratio the precipitate becomes very gelatinous or gummy and does not disperse on stirring. Passing through this point in either direction changes the precipitate back to its original form.

Magnesium hydride free of aluminum was obtained using the conditions reported by Schlesinger only when the reaction time was extended to 3 days at room temperature. It was also determined that the $(C_2H_5)_2Mg$ concentration cannot exceed 1 M when using $LiAlH_4$ solution of 1.5 M concentration, if aluminum is to be excluded from the magnesium hydride. The aluminum free magnesium hydride still contains about 16% diethyl ether. No attempt has been made to completely desolvate the magnesium hydride.

A possible intermediate in this reaction may be C_2H_5MgH. Such a compound could possibly be prepared by simply adjusting the stoichiometry of the reaction of $LiAlH_4$ and $(C_2H_5)_2Mg$ appropriately.

$$LiAlH_4 + 4(C_2H_5)_2Mg \rightarrow 4\ C_2H_5MgH + LiAl(C_2H_5)_4 \qquad (9)$$

Coates[9] recently attempted to prepare C_2H_5MgH by the reaction of $(C_2H_5)_2Mg$ with $NaB(C_2H_5)_3H$. When an experiment was carried out at the proper ratio of $LiAlH_4$:$(C_2H_5)_2Mg$ (0.25:1) to produce C_2H_5MgH, the precipitate from the reaction proved to be magnesium hydride as shown by elemental and infrared analysis. The filtrate still contained $(C_2H_5)_2Mg$ as shown by the infrared spectrum (νC-Mg 512 cm^{-1}), and elemental analysis showed that almost half of the starting magnesium was still in solution. The reaction is then described by equation 10 rather than equation 9.

$$LiAlH_4 + 4(C_2H_5)_2Mg \rightarrow 2\ MgH_2 + LiAl(C_2H_5)_4 + 2\ (C_2H_5)_2Mg \qquad (10)$$

If C_2H_5MgH is an intermediate in the reaction, it either reacts faster than $(C_2H_5)_2Mg$ with $LiAlH_4$ or disproportionates rapidly to $(C_2H_5)_2Mg$ and MgH_2.

The magnesium hydride formed using an excess of $(C_2H_5)_2Mg$ contains some quantity of aluminum impurity initially that is gradually eliminated over a period of several days. A plausible explanation is that during the precipitation

of magnesium hydride some aluminum species is occluded in the polymeric structure. The occluded material could be removed by a process of dissolution and reprecipitation of the magnesium hydride. Since MgH_2 is totally insoluble in diethyl ether, and since with excess $LiAlH_4$, the MgH_2 always contains some aluminum impurity, it seems possible that a complex may be formed between MgH_2 and $(C_2H_5)_2Mg$. A complex between $(C_2H_5)_2Mg$ and MgH_2 would be the same as associated C_2H_5MgH. An experiment was performed in which a slurry of MgH_2 was stirred overnight with a large excess of diethylmagnesium in diethyl ether. An infrared spectrum of the supernatant showed that only $(C_2H_5)_2Mg$ was present in solution. If a complex is being formed, it is present in very low concentration.

Further study on the aluminum impurity indicates that it may not be occluded material, but rather that a reaction between MgH_2 and the lithium hydridoalkylalanate species is occurring.

$$MgH_2 + LiAl(C_2H_5)_nH_{4-n} \rightleftarrows LiH + H\text{-}Mg\text{-}Al(C_2H_5)_nH_{4-n} \quad (11)$$

$$MgH_2 + 2\ LiAl(C_2H_5)_nH_{4-n} \rightleftarrows 2\ LiH + Mg[Al(C_2H_5)_nH_{4-n}]_2 \quad (12)$$

Since some of the reactants and products are insoluble, the attainment of equilibrium should be very slow. The equilibrium lies largely to the left except at high concentration of the $LiAl(C_2H_5)_nH_{4-n}$ species. If the concentration of $(C_2H_5)_2Mg$ exceeds 1 M when reacting with a $LiAlH_4$ solution of 1.5 M, the MgH_2 formed with excess $(C_2H_5)_2Mg$ contains aluminum even after a reaction time of 5 days (0.23 Al:1 Mg). Lithium analysis of the MgH_2 containing aluminum impurity indicates a ratio of lithium to aluminum greater than one. In some cases the ratio is as high as 2.00 Li:1 Al. Also in some cases a small quantity of magnesium is found in solution that can only be there

as $Mg[Al(C_2H_5)_nH_{4-n}]_2$ since the infrared spectra show no C-Mg bands at 512 cm^{-1}.

To investigate this question further two reactions were performed using magnesium hydride with only a small amount of aluminum impurity (0.004 Al:1 Mg). The MgH_2 was stirred overnight with $LiAlH_4$ and $LiAl(C_2H_5)_4$ solutions in ether. The amount of aluminum in each case increased greatly. Also in the $LiAl(C_2H_5)_4$ reaction the magnesium hydride looked very much like the gummy material formed at 0.5:1 ratio of $LiAlH_4$:$(C_2H_5)_2Mg$. Although these experiments indicate that some reaction may be occurring between $LiAl(C_2H_5)_nH_{4-n}$ species and MgH_2, further work is needed to clarify the problem.

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CONCERNING THE PREPARATION OF MAGNESIUM ALUMINUM HYDRIDE. A STUDY OF THE REACTIONS OF LITHIUM AND SODIUM ALUMINUM HYDRIDE WITH MAGNESIUM HALIDES IN ETHER SOLVENTS

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Abstract

The reactions of Alkali metal alumino-hydrides with magnesium halides in ether solvents were investigated as possible routes to magnesium aluminum hydride [$Mg(AlH_4)_2$]. The ability of these reactions to produce $Mg(AlH_4)_2$ depended on the nature of the alkali-metal, the halide, the solvent and the solubility of the alkali-metal halide by-product.

Although $Mg(AlH_4)_2$ was previously reported prepared by the reaction of $LiAlH_4$ and magnesium bromide in diethyl ether, this reaction regardless of the nature of the halogen or solvent was found to produce an equilibrium mixture ($LiAlH_4 + MgBr_2 = LiBr + BrMgAlH_4$) which varied in its composition depending on the amount of $LiAlH_4$ used, but which did not contain any detectable amount of $Mg(AlH_4)_2$.

$Mg(AlH_4)_2$ was prepared from $NaAlH_4$ and $MgCl_2$; however, the by-product NaCl could only be removed from the hydride after prolonged extraction of the hydride with ether solvent.

Magnesium Aluminum hydride as the tetrakis tetrohydrofuran solvate was prepared halogen free by the reaction of sodium aluminum hydride and magnesium iodide in a mole ratio of two to one. Halogenomagnesium aluminum hydrides ($XMgAlH_4$) were prepared in tetrahydrafuran by the reaction of sodium aluminum hydride and the magnesium halide in one to one stoichiometry.

INTRODUCTION

The preparation of magnesium aluminum hydride ($Mg(AlH_4)_2$) was first reported in 1950 by Wiberg and Bauer.[2,3,4,5] The preparation of this

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new hydride was reported by three different synthetic routes.

$$4\ MgH_2 + 2\ AlCl_3 \rightarrow Mg(AlH_4)_2 + 2\ MgCl_2 \quad (1)$$

$$MgH_2 + 2\ AlH_3 \rightarrow Mg(AlH_4)_2 \quad (2)$$

$$2\ LiAlH_4 + MgBr_2 \rightarrow Mg(AlH_4)_2 + 2LiBr \quad (3)$$

Magnesium hydride (MgH_2) was reported to react with both aluminum hydride (AlH_3) and aluminum chloride ($AlCl_3$) in diethyl ether to produce $Mg(AlH_4)_2$ whereas the third method involved the reaction of lithium aluminum $LiAlH_4$ with $MgBr_2$ in diethyl ether. The $Mg(AlH_4)_2$ produced was reported to be

soluble in diethyl ether and to decompose at 140°, however few experimental details concerning the preparations were given.

Hertwig[6] reported the preparation of $Mg(AlH_4)_2$ by hydrogenolysis of a

(6) Hertwig, A., German Patent 921, 986 (1955)

Grignard reagent in diethyl ether followed by the addition of aluminum chloride to the reaction product. The following series of reactions were suggested to describe the course of the reaction.

$$4\ RMgX + AlX_3 + 4\ H_2 \rightarrow XMgAlH_4 + 3\ MgX_2 + 4\ RH \quad (4)$$

$$3\ RMgX + AlX_3 + 3\ H_2 \rightarrow AlH_3 + 3\ MgX_2 + 3\ RH \quad (5)$$

$$2\ XMgAlH_4 \rightarrow Mg(AlH_4)_2 + MgX_2 \quad (6)$$

However again few experimental details were given. In this connection Becker and Ashby[7,8] reported that hydrogenolysis of Grignard reagents

(7) Becker, W. E. and Ashby, E. C., J. Org. Chem. 29, 954 (1964)

(8) Becker, W. E. and Ashby, E. C., Inorg. Chem. 4, 1816 (1965)

produces a mixture of MgH_2 and magnesium halide. Therefore, the MgH_2 produced in the hydrogenolysis reaction reported by Hertwig could have reacted with $AlCl_3$ to form $Mg(AlH_4)_2$ in a similar way to that previously reported by Wiberg. The suggested $XMgAlH_4$ could then have arisen from the redistribution of $Mg(AlH_4)_2$ and $MgCl_2$.

Sometime ago we prepared $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$ in dimethyl ether[9] and noticed that the physical properties of this compound

(9) Ethyl Corp. British Patent. 905, 985 (1962).

were different from the properties reported by Wiberg for $Mg(AlH_4)_2$. The $Mg(AlH_4)_2$ prepared by us was insoluble in diethyl ether and decomposed at 180°C.

In 1966 Czech workers[10] reported the preparation of $Mg(AlH_4)_2$ in THF

(10) J. Plesek and S. Hesmanch, Col. Czech. Chem. Comm. 31, 3060 (1966)

by the reaction of $NaAlH_4$ and $MgCl_2$. However no infrared or X-ray powder diffraction data was given.

It would appear that there is some confusion in the literature concerning the preparation and properties of $Mg(AlH_4)_2$. Since the reaction of $MAlH_4$ and MgX_2 in ethers to produce $Mg(AlH_4)_2$ is so fundamental to hydride chemistry, we decided to study this reaction in diethyl ether and THF in detail.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen (MnO) and water plus solvents (Dry ice-acetone) or on the bench under nitrogen. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer model 621 Infrared spectrophotometer. Sodium chloride cells were used. Spectra of solids were obtained in nujol which had been dried over sodium wire and stored in a dry box. No change was observed in the spectra of

either solutions or mulls after standing in the cell for sometime. It is therefore concluded that no interaction of the products studied with the cell windows takes place.

X-ray powder diffraction patterns were run on a Debye-Scherrer camera of 114.6 mm diameter using CuK (1.540A°) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately before use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Diethyl ether and THF solutions of these complex metal hydrides were prepared by adding appropriate amounts of the hydride to a 1000 ml round bottom flask containing a large magnetic stirring bar and then distilling the solvent onto the hydride. The solutions were then stirred overnight and filtered through dried celite analytical filter aid. The resulting clear solutions were standardized by EDTA titration of aluminum.

Preparation of Magnesium Halides in diethyl ether and THF.[11,12] - In a typical

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(11) B. K. Lewis, Dissertation Abstr., 20 (1960) 2544

(12) E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 14 (1968) 1

preparation of MgX_2 in ether solvents, 2 gm of Magnesium was added to 20 gm of Mercuric Chloride in a 500 ml round bottom flask with a magnetic stirring bar. Two hundred and fifty milliliters of THF was then distilled onto the mixture. The solution was stirred overnight and filtered. The solutions were then standardized by magnesium analysis (EDTA) and halogen analysis (Volhard method). The magnesium to halogen ratio was 1.0:1.97.

A qualitative test for residual mercury in the solutions was negative using ferrocyanide and 2,2'-dipyridyl. The solutions were also tested for solvent impurities by hydrolyzing a sample of the solution with distilled water in benzene. The organic matter was then salted out of the water layer into the benzene. A sample of the benzene layer was then analyzed by VPC. These tests showed only diethyl ether to be present in the original solution of MgX_2.

An exception to this procedure was the preparation of magnesium chloride in diethyl ether. Anhydrous hydrogen chloride in diethyl ether was added to a diethyl ether solution of ethyl magnesium chloride. The precipitate formed was washed with diethyl ether and dried under vacuum. The solid gave the following analysis: Mg: Cl: $(C_2H_5)_2O$; 1.0: 1.98: 1.02.

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis was carried out by titration with EDTA. If aluminum was present, it was masked with triethanol amine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample and measuring the volume of gas evolved after passing it through dry-ice acetone to remove ether. The amount of ether solvated to a compound was assumed by difference.

General Procedures for Infrared Studies. - A measured amount of magnesium halide in solution was added to a 3 neck 500 ml round bottom flask equipped with a 3 way stopcock, and addition funnel, and a dry ice condenser. The solution of alkali metal aluminum hydride was added in a stepwise fashion to $MAlH_4$:MgX_2 mole ratios of 0.5:1.0; 1.0:1.0; 1.5:1.0; 2.0:1.0; 3.0:1.0. After each addition the solution was stirred for fifteen minutes and any precipitate formed was allowed to settle. A sample of the supernatent liquid was taken with a syringe through the three way stopcock (under strong nitrogen flush) and the infrared cell filled in the dry box.

Reaction of Sodium Aluminum hydride and Magnesium Chloride in THF. - At the 0.5:1.0 addition a precipitate was formed. The infrared spectrum of the solution showed bands at 1715 cm^{-1}, 795 cm^{-1}, and 760 cm^{-1}. At the 1.0:1.0 addition, these bands increased in intensity and more precipitate was formed. Elemental analysis and an X-ray powder pattern of this solid showed it to be NaCl. At the 1.5:1.0 addition the intensity of the infrared bands decreased and more precipitate was formed. At 2.0:1.0 ratio, no infrared bands appeared in the Al-H stretching and deformation regions and more precipitate formed. In a separate experiment the solid was filtered at this point and analyzed. The Cl:Mg:Al:H ratio formed was 2.0:1.02:2.03:7.80. At 3.0:1.0 addition bands appeared at 1680 cm^{-1} and 772 cm^{-1}. No more precipitate was formed. Sodium Aluminum hydride in THF gave bands at 1680 cm^{-1} and 772 cm^{-1}.

The X-ray powder pattern of the solid showed NaCl to be present as well as some other substance. The mull of the solid gave bands at 1725 cm^{-1}; 1025 cm^{-1}; 920 cm^{-1}; 875 cm^{-1}; 740 cm^{-1}.

Sodium Aluminum hydride and Magnesium bromide in THF. - The reaction of $NaAlH_4$ and $MgBr_2$ in THF was followed by infrared analysis. The results were

similar to those reported for the previous system.

Sodium Aluminum hydride and Magnesium Iodide in THF. - At 0.5:1.0 addition, a precipitate formed and a weak band at 1730 cm^{-1} appeared. At 1.0:1.0 addition, more solid was formed and there a shoulder appeared on the low frequency side of the band at 1730 cm^{-1} although its intensity is not increased. Analysis of the 1.0:1.0 solid gave I:Mg:Al ratio of 2.09:1.58:1.0. The X-ray powder pattern of the solid showed it to be a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$. Further addition of $NaAlH_4$ increased the intensity of the shoulder until at a ratio of 10:1.0 the entire band is centered at 1680 cm^{-1}. The solid at 10:1.0 addition gave the following analysis: Mg:Al:I:THF; 1.0:1.94:0:4.01. Infrared and X-ray powder pattern data are given in Tables I and II.

Lithium Aluminum Hydride and Magnesium Chloride in THF. - At 0.5:1.0 addition, infrared analysis shows bands at 1715 cm^{-1}, 795 cm^{-1} and 760 cm^{-1}. At 1.0:1.0 addition, these bands increase in intensity and broaden somewhat. At the 1.5:1.0 addition the bands increase in intensity and a shoulder appears at the low frequency side of the 1715 cm^{-1} band. At 2.0:1.0 addition, these bands have increased in intensity and at 3.0:1.0 addition, what was the shoulder in the previous addition has become the main band and is centered around 1691 cm^{-1}. The band at 760 cm^{-1} broadened and its intensity increased to a greater extent than the 795 cm^{-1} band. ($LiAlH_4$ in THF has bands at 1691 cm^{-1} and 763 cm^{-1}). No precipitate is observed even out to the 3.0:1.0 addition.

Lithium Aluminum hydride and Magnesium Bromide in THF. - Similar results were obtained as in the previous system. No precipitate was observed even to a $LiAlH_4$ to $MgBr_2$ ratio of 5.0:1.0.

Lithium Aluminum Hydride and Magnesium Iodide in THF. - No bands appeared in the infrared spectrum of the solution which are different from those of THF until a $LiAlH_4$:MgI_2 ratio of greater than 2.0:1.0 is attained. At this point bands at 1691 cm^{-1} and 765 cm^{-1} appeared. An analysis of the precipitate gave Mg:Al:I ratios of 1.0:1.80:0.087. The X-ray powder diffraction pattern showed $Mg(AlH_4)_2 \cdot 4THF$.

Lithium Aluminum hydride and Magnesium Bromide in diethyl ether. - At 0.5:1.0 addition of $LiAlH_4$ to $MgBr_2$, bands appear in the infrared spectrum of the solutions at 1780 cm^{-1} and 755 cm^{-1}. At 1.0:1.0 addition, a shoulder on the low frequency side of the 1780 cm^{-1} band appears. At 1.5:1.0 addition, the bands increased in intensity and the band at 755 broadened. At 2.0:1.0 addition, bands at 1780 cm^{-1} and 1740 cm^{-1} were of equal intensity. At the 3.0:1.0 addition the bands at 1740 cm^{-1} increased in intensity.

A precipitate was initially formed which gave an indefinite analysis. However it contained only 2 % of the total Magnesium.

Lithium Aluminum hydride and Magnesium Iodide in diethyl ether. - No bands other than diethyl ether appeared up to a $LiAlH_4$:MgI_2 ratio of 1.0:1.0. A white solid was obtained up to this ratio which gave the following analysis: I:Mg:Al:Et_2O; 0.99:1.0:1.01:1.0. Addition of more $LiAlH_4$ gave infrared bands corresponding to $LiAlH_4$.

Sodium Aluminum hydride and Magnesium Bromide in diethyl ether. - Magnesium bromide in diethyl ether was added to $NaAlH_4$ in a ratio of 1.0:2.0. The solution was stirred for four days. At the end of this time no bands in the Al-H stretching and deformation regions were found in the infrared spectrum of the solution. An X-ray powder pattern of the solid showed lines due to

NaBr and some other compound which was not $MgBr_2$ or $NaAlH_4$. The infrared spectrum of the solid had bands at 1800 cm^{-1}; 1285 cm^{-1}; 1190; 1150; 1090; 1045; 995; 845 and 740 cm^{-1}. It produced a Mg:Al:Br ratio of 1.0:2.12:2.2.

Lithium Aluminum hydride and Magnesium Chloride in Diethyl ether. - Lithium Aluminum hydride in diethyl ether was added to $MgCl_2$ in diethyl ether in a mole ratio of 2.0:1.0. The solution was stirred for two days. The solid obtained gave the following analysis: Cl:Mg:Al; 12:1.0:2.16. The X-ray powder pattern showed only LiCl. The infrared spectrum of the solid gave no definite bands in the Al-H stretching region. After removing some of the solvent from the filtrate a solid was obtained which gave the following analysis: Li:Mg:Al:Cl; 1.0:1.1:1.9:1.0. The X-ray powder pattern gave lines for LiCl and some other compounds. The infrared spectrum of the solid gave bands at 1845 cm^{-1}; 1780 cm^{-1}; 1190 cm^{-1}; 1150 cm^{-1}; 1090 cm^{-1}; 1040 cm^{-1}; 995 cm^{-1}; 900 cm^{-1}.

When $LiAlH_4$ was added to $MgCl_2$ in diethyl ether in a mole ratio of 1.0:1.0, the precipitate obtained gave the following analysis: Li:Mg:Al:Cl; 3.2:1.0:1.5:4.4. The X-ray powder pattern showed lines for LiCl and another compound which didn't correspond to the compound in the 2:1 case. The solid obtained by removing the solvent from the filtrate gave the following analysis: Li:Cl:Mg:Al; 0.5:1.7:1.5:1.1. The X-ray powder pattern gave lines for LiCl. In addition to the lines for LiCl other lines were observed which corresponded to the second solid in the 2:1 case. The infrared spectrum of this solid gave bands at 1800 cm^{-1}; 1260; 1195; 1150; 1095; 1045; 1000; and 900 cm^{-1}. The solution spectrum of the 2:1 and 1:1 case both gave bands at 1780 cm^{-1} and shoulders on the low frequency side.

General Procedure for the isolation of Intermediates. - The Alkali metal

aluminohydride was added to the magnesium halide in a ratio of 1.0:1.0. Any solid initially formed was filtered, analyzed, and its infrared spectrum and X-ray powder pattern obtained. The resulting solutions were then fractionally crystallized and the solids obtained were analyzed, and their infrared spectrum and X-ray powder pattern obtained.

Chloromagnesium Aluminum hydride in THF. - When $NaAlH_4$ was added to $MgCl_2$ in a mole ratio of 1.0:1.0 a precipitate formed which was filtered. The resulting filtrate was then subjected to crystallization by solvent removal. The solid obtained gave the following analysis: Cl:Mg:Al:H:THF; 0.97:1.0:0.96:4.07:3.75. The infrared spectrum of this solid in nujol gave bands at 1730 cm^{-1}; 1030 cm^{-1}; 920 cm^{-1}; 880 cm^{-1} and 745 cm^{-1}. For the major lines in the X-ray powder pattern see Table II.

In the reaction of lithium aluminum hydride and $MgCl_2$ in THF, similar results were obtained.

Bromo Magnesium Aluminum Hydride in THF. - The solutions containing $NaAlH_4$ and $MgBr_2$ in a mole ratio of 1.0:1.0 were treated in the same way as the $ClMgAlH_4$ solution. The solid material obtained upon crystallization gave the following analysis: Br:Mg:Al:H:THF of 1.0:1.08:1.05:3.99:3.77. The infrared spectrum of this solid in nujol gave bands at 1715 cm^{-1}; 1030 cm^{-1}; 915 cm^{-1}; 875 cm^{-1}; 795 cm^{-1} and 745 cm^{-1}. The X-ray powder pattern is shown in Table II.

The reaction of $LiAlH_4$ and $MgBr_2$ in THF produced similar results.

Magnesium Aluminum Hydride in THF. - Analysis of the compound prepared from $NaAlH_4$ and $MgCl_2$ in 2.0:1.0 ratio in THF gave a Mg:Al:H:THF ratio of 1.05:2.0:8.10:3.80. The infrared spectrum of a saturated solution in THF gave weak bands at 1730 cm^{-1}; 800 cm^{-1} and 750 cm^{-1}. The infrared spectrum of the solid

in nujol gave bands at 1725 cm^{-1}; 1035 cm^{-1}; 935 cm^{-1}; 890 cm^{-1} and 760 cm^{-1}. The X-ray powder diffraction patterns are given in Table II.

Magnesium Aluminum hydride in Diethyl Ether. - Analysis of this compound gave Mg:Al:H:Et_2O. There was no solution spectrum. The infrared spectrum of the solid in nujol produced bands at: 1800 cm^{-1}; 1285 cm^{-1}; 1190 cm^{-1}; 1150 cm^{-1}; 1090 cm^{-1}; 1045 cm^{-1}; 995 cm^{-1}; 845 cm^{-1}; 740 cm^{-1}. The X-ray powder diffraction pattern is given in Table II.

Bromo Magnesium Aluminum Hydride in Diethyl Ether. - Lithium Aluminum hydride in diethyl ether was added to $MgBr_2$ in a mole ratio of 1.0:1.0. The solvent was then removed and the solid obtained gave the following analysis: Li:Al:Mg:Br; 1.1:1.0:1.1:2.13. The X-ray powder pattern showed LiBr but not $LiAlH_4$ or $MgBr_2 \cdot Et_2O$. The infrared spectrum of the solid in nujol gave bands at 1825 cm^{-1}; 900 cm^{-1}; 755 cm^{-1}; and 720 cm^{-1}. An initial solid gave a band at 1870 cm^{-1}.

Magnesium Aluminum hydride and Magnesium Chloride in THF. - When equimolar amounts of $Mg(AlH_4)_2$ and $MgCl_2$ in THF were mixed, the resulting solution gave an infrared spectrum corresponding to $ClMgAlH_4$. The removal of the solvent gave a solid whose elemental analysis; infrared spectrum and X-ray powder pattern were identical to $ClMgAlH_4 \cdot 4THF$.

Lithium Bromide and Magnesium Aluminum hydride in Diethyl Ether. - When equimolar amounts of LiBr and $Mg(AlH_4)_2$ were mixed in diethyl ether the resulting solution gave bands at 1780 cm^{-1}; 1740 cm^{-1} (both of equal intensity) and at 793 cm^{-1} and 762 cm^{-1}. See Figure 1.

Results and Discussion

In the present study $LiAlH_4$ and $NaAlH_4$ were allowed to react with $MgCl_2$, $MgBr_2$ and MgI_2 in diethyl ether and THF. It is important that this reaction was studied in such detail since the course of the reaction is dependent on the nature of the alkali metal, the halide, the solvent and the solubilities of the alkali metal by-product. The discussion will be divided roughly into two parts, namely, those combinations of reactants that produce $Mg(AlH_4)_2$ as the reaction product and those combinations of reactants that either stop the $XMgAlH_4$ or produce a mixture of products.

When $NaAlH_4$ was allowed to react with $MgCl_2$ in THF in a mole ratio of 1.0:1.0, a white precipitate appeared which was shown by elemental and X-ray powder pattern analyses to be NaCl. The infrared spectrum of the reaction solution showed bands at 1715 cm^{-1}; 795 cm^{-1} and 760 cm^{-1}. None of these bands correspond to $NaAlH_4$, but are characteristic of Al-H stretching and deformation. When this solution was subjected to fractional crystallization, successive fractions gave elemental analyses corresponding to the empirical formula $ClMgAlH_4 \cdot 4THF$. The X-ray powder pattern of this solid shows no lines due to $MgCl_2 \cdot 2THF$; $Mg(AlH_4)_2 \cdot 4THF$; $NaAlH_4$ or NaCl. Furthermore, the infrared spectrum of this solid shows bands at 1730 cm^{-1}; 1030 cm^{-1}; 920 cm^{-1}; 880 cm^{-1}; 745 cm^{-1} which are not characteristic of either $MgCl_2$ or $Mg(AlH_4)_2 \cdot 4THF$. Also no bands characteristic of Mg-H were observed. It would appear then that the product produced in this reaction is $ClMgAlH_4 \cdot 4THF$ and not a physical mixture of $MgCl_2$ and $Mg(AlH_4)_2$ or $MgCl_2$, MgH_2 and AlH_3.

As one adds more $NaAlH_4$ to the $MgCl_2$ in THF until the mole ratio is 2.0:1.0, more precipitate is formed and the infrared spectrum of the solution

shows no bands in the Al-H or Mg-H stretching and deformation regions. The infrared spectrum of this solid in nujol shows bands at 1725 cm^{-1}; 1025 cm^{-1}; 920 cm^{-1}; 875 cm^{-1}; 785 cm^{-1}; 740 cm^{-1}. The X-ray powder pattern of the solid showed NaCl in admixture with some other compound. The elemental analysis of the solid was consistent with a mixture of NaCl and $Mg(AlH_4)_2$. Soxhlet extraction of this solid with THF yielded crystals which produced an analysis consistent with $Mg(AlH_4)_2 \cdot 4THF$. The infrared spectrum of the extracted product was the same as the mixture and the X-ray powder pattern showed all the lines of the mixture after subtracting out the lines due to NaCl. The infrared and powder pattern data of the extracted solid were not consistent with the description of the product as a physical mixture of MgH_2 and AlH_3.

$$NaAlH_4 + MgCl_2 \xrightarrow{THF} ClMgAlH_4 + NaCl \quad (7)$$

$$2\ NaAlH_4 + MgCl_2 \xrightarrow{THF} Mg(AlH_4)_2 + 2\ NaCl \quad (8)$$

When $MgCl_2$ in THF was added to $Mg(AlH_4)_2 \cdot 4THF$, the resultant solution produced an infrared spectrum corresponding to $ClMgAlH_4$. Fractional crystallization of the solution yielded solid fractions whose analyses, X-ray powder patterns and infrared analyses were consistent with $ClMgAlH_4 \cdot 4THF$ prepared from $NaAlH_4$ and $MgCl_2$ in THF in 1:1 stoichiometry.

$$MgCl_2 + Mg(AlH_4)_2 \xrightarrow{THF} 2\ ClMgAlH_4 \quad (9)$$

Since the reaction of $NaAlH_4$ with $MgCl_2$ in THF is probably a stepwise reaction to produce $ClMgAlH_4$ and then $Mg(AlH_4)_2$, any $Mg(AlH_4)_2$ formed in the initial stages of the reaction would rapidly redistribute with $MgCl_2$ to form $ClMgAlH_4$.

When $NaAlH_4$ was allowed to react with $MgBr_2$ in THF results similar to the reactions with $MgCl_2$ were observed, i.e., at 1:1 ratio $BrMgAlH_4$ was formed and

at 2:1 ratio $Mg(AlH_4)_2$ was formed. Since sodium bromide is also insoluble in THF, $Mg(AlH_4)_2$ produced in this reaction contains two molar equivalents of NaBr.

Magnesium Aluminum hydride could be prepared essentially halogen free by reacting $NaAlH_4$ and MgI_2 in THF at a mole ratio of 10:1.0. Since the NaI by product is soluble in THF, $Mg(AlH_4)_2$ precipitates from solution halogen free. Attempts to prepare $IMgAlH_4$ in THF were unsuccessful due to the disproportionation of this compound to MgI_2 and $Mg(AlH_4)_2$ in THF. This was demonstrated further by adding $IMgAlH_4 \cdot Et_2O$ to THF. The reaction was very exothermic and the resultant solid produced an infrared spectrum and X-ray powder pattern consistent with a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$.

$$NaAlH_4 + MgI_2 \xrightarrow{THF} NaI + [IMgAlH_4] \rightarrow 1/2\ MgI_2 + 1/2\ Mg(AlH_4)_2 \qquad (10)$$

A second reaction which produces $Mg(AlH_4)_2$ essentially halogen free is that between $LiAlH_4$ and MgI_2 in THF at a mole ratio of three or four to one. Here again the disproportionation of $IMgAlH_4$ to MgI_2 and $Mg(AlH_4)_2$ as well as the insolubility of the $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$ prevents the isolation of $IMgAlH_4$ in THF. The solubility of the LiI by-product enables the $Mg(AlH_4)_2$ to be obtained halogen free.

$$2\ LiAlH_4 + MgI_2 \rightarrow Mg(AlH_4)_2 + 2\ LiI \qquad (11)$$

When $NaAlH_4$ was allowed to react with $MgBr_2$ in diethyl ether at a mole ratio of 2.0:1.0 a white precipitate formed. This solid was shown by X-ray powder diffraction and I.R. to be a mixture of NaBr and $Mg(AlH_4)_2$.

$$2\ NaAlH_4 + MgBr_2 \xrightarrow{Et_2O} Mg(AlH_4)_2 + 2\ NaBr \qquad (12)$$

The reactions described until now have been reasonably straight forward. When the alkali metal aluminum hydrides were added to the MgX_2 in 1:1 stoichiometry, $XMgAlH_4$ was formed. Upon addition of more $MAlH_4$, the $XMgAlH_4$ reacted further to form $Mg(AlH_4)_2$. In most of these cases the insolubility of the alkali metal halide by-product or of the MgI_2 seems to play an important role. If now we concentrate on the reactions where the alkali metal halide is soluble, we see that the reaction proceeds in a somewhat different fashion.

When $LiAlH_4$ was allowed to react with $MgCl_2$ in THF in 1.0:1.0 ratio, the reaction filtrate exhibited infrared absorption bands corresponding to $ClMgAlH_4$ as was observed in the reaction of $MgCl_2$ with $NaAlH_4$ in THF. No precipitate formed in the reaction since LiCl is soluble in THF. When the 1.0:1.0 ratio was exceeded the bands due to $ClMgAlH_4$ didn't decrease in intensity as in the previous cases. Instead as more $LiAlH_4$ was added, bands due to the $LiAlH_4$ increased in intensity. Thus, instead of $Mg(AlH_4)_2$ being produced, an equilibrium resulted as shown in Eq. 13.

$$LiAlH_4 + MgCl_2 \overset{THF}{\rightleftharpoons} ClMgAlH_4 + LiCl \qquad (13)$$

In order to determine if $ClMgAlH_4$ was the actual species being formed, $LiAlH_4$ was added to $MgCl_2$ in THF in a 1:1 ratio. The solution was then fractionally crystallized and the resulting solids subjected to X-ray, infrared and elemental analyses. All of the analyses showed that $ClMgAlH_4 \cdot 4THF$ and LiCl were the major products present.

Similar results were obtained when $LiAlH_4$ and $MgBr_2$ were allowed to react in THF. The products of this reaction are $BrMgAlH_4 \cdot 4THF$ and LiBr. Here no solid was formed in the reaction even when the $LiAlH_4$:$MgBr_2$ ratio was 5.0:1.0. (LiBr is soluble in THF).

The reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether also showed this equilibrium behavior. The equilibrium in diethyl ether may not lie as far to the right as in THF since the $LiAlH_4$ appears in the solution spectrum sooner than in THF. A small amount of initial precipitate was formed, however it was found to contain less than 2% of the total magnesium in the reaction. No additional precipitate was formed even at a $LiAlH_4$:$MgBr_2$ ratio of 3:1.

In order to test the equilibrium hypothesis an ether solution of LiBr was added to $Mg(AlH_4)_2$ obtained by the reaction of $NaAlH_4$ and $MgBr_2$ in diethyl ether. The resulting solution gave bands of equal intensity at 1780 cm^{-1} and 1740 cm^{-1}. ($LiAlH_4$ in ether has a band at 1740 and was identical to a solution of $BrMgAlH_4$ and $LiAlH_4$). The spectrum was also identical to the solution spectrum of the 2.0:1.0 addition product of $LiAlH_4$ to $MgBr_2$.

$$LiBr + Mg(AlH_4)_2 \xrightarrow{Et_2O} BrMgAlH_4 + LiAlH_4 \quad (14)$$

$$LiAlH_4 + MgBr_2 \xrightarrow{Et_2O} BrMgAlH_4 + LiBr \quad (15)$$

In diethyl ether the reaction of $LiAlH_4$ with MgI_2 was also found to be a special case. At a stoichiometry of 1:1, a white solid was obtained which was shown by infrared, X-ray powder diffraction and elemental analyses to be $IMgAlH_4 \cdot Et_2O$. Further addition of $LiAlH_4$ did not produce $Mg(AlH_4)_2$.

$$LiAlH_4 + MgI_2 \xrightarrow{Et_2O} IMgAlH_4 + LiI \quad (16)$$

The results of the reaction of $LiAlH_4$ and $MgCl_2$ in diethyl ether are somewhat confusing. There is evidence that both $ClMgAlH_4$ and $Mg(AlH_4)_2$ are formed. Both the 1:1 and 2:1 reaction mixtures appear to contain $ClMgAlH_4$. In the 2:1 case there is evidence also that some $Mg(AlH_4)_2$ is formed.

Infrared studies in the solid state of the compounds studied indicate that the degree of covalent bonding between the magnesium and the tetrahydroaluminate group is dependent upon the degree of solvation. This is especially true in the case of the tetrahydrofuran solvates.

Both $Mg(AlH_4)_2$ and $ClMgAlH_4$ are obtained from THF solution as the tetrakis tetrahydrofuranates. It seems more reasonable to conclude that the solvated THF is solvating the magnesium rather than the AlH_4 group. In addition to magnesium being a better lewis acid than AlH_4 toward THF, there is also very little evidence for AlH_4 solvation by THF in other systems, e.g., $LiAlH_4$, $NaAlH_4$ or R_4NAlH_4. It is interesting that $NaAlH_4$ and R_4NAlH_4 precipitate from THF solution as non-solvates. In the case of $LiAlH_4$, it appears that the THF is solvating the lithium.

The Al-H stretching frequencies in both $Mg(AlH_4)_2$ and $ClMgAlH_4$ are very nearly the same. (1725 cm^{-1} and 1730 cm^{-1} respectively). Therefore, the environment around the AlH_4 must be very nearly the same in both cases. Since the number of AlH_4 groups is different, one might expect that the number of solvated THF molecules would be different. However, in both cases they are the same, i.e., four. Thus it seems more reasonable to place all four of the THF solvate molecules on the magnesium in a tetrahedral arrangement. This should make both $Mg(AlH_4)_2$ and $ClMgAlH_4$ more ionic, since the lewis acidity of the Magnesium is satisfied by the THF.

The solid state infrared spectrum of $Mg(AlH_4)_2 \cdot 4THF$ and $ClMgAlH_4 \cdot 4THF$ both exhibit single sharp bands at 1725 and 1730 cm^{-1} respectively. Since the bands are not split the four hydrogens on the AlH_4 group must be equivalent with

no bridging. This would be consistent with the ionic model.

One can remove two of the solvate THF molecules very easily. The infrared spectrum of the resulting solid shows that the Al-H stretching band has moved to a higher frequency and split into two bands at 1785 cm^{-1} and 1730 cm^{-1}. This indicates that the compound has become more covalent, and that there are probably bridging hydrogens as indicated by the two bands. If one desolvates $Mg(AlH_4)_2$ completely, the Al-H stretching frequency shifts to an even higher frequency and remains split with bands at 1855 cm^{-1} and 1830 cm^{-1}.

When $ClMgAlH_4 \cdot 4THF$ is dissolved in benzene and recrystallized, the solid obtained contains only two THF solvate molecules. The infrared spectrum of this solid shows that the Al-H stretching band has shifted to a higher frequency. However, the band is not split, although it is somewhat broad and is centered at 1775 cm^{-1}. Upon complete desolvation the Al-H stretching band again shifts to a higher frequency and this time splits into two bands; 1850 and 1830 cm^{-1}.

These data indicate that upon desolvation the $Mg(AlH_4)_2$ and $ClMgAlH_4$ exhibited more covalent character through bridging hydrogens. Lithium Aluminum hydride in the solid state, which is considered to be covalent, has two bands in the solid state infrared spectrum at 1770 and 1625 cm^{-1}.

Acknowledgements. - We are indebted to the National Aeronautics and Space Administration (Grant NAG-657) and the Office of Naval Research (Contract N00014-67-A-0159-0005) for their support of this work.

We would also like to thank Dr. J. A. Bertrand for the use of his X-ray powder diffraction equipment.

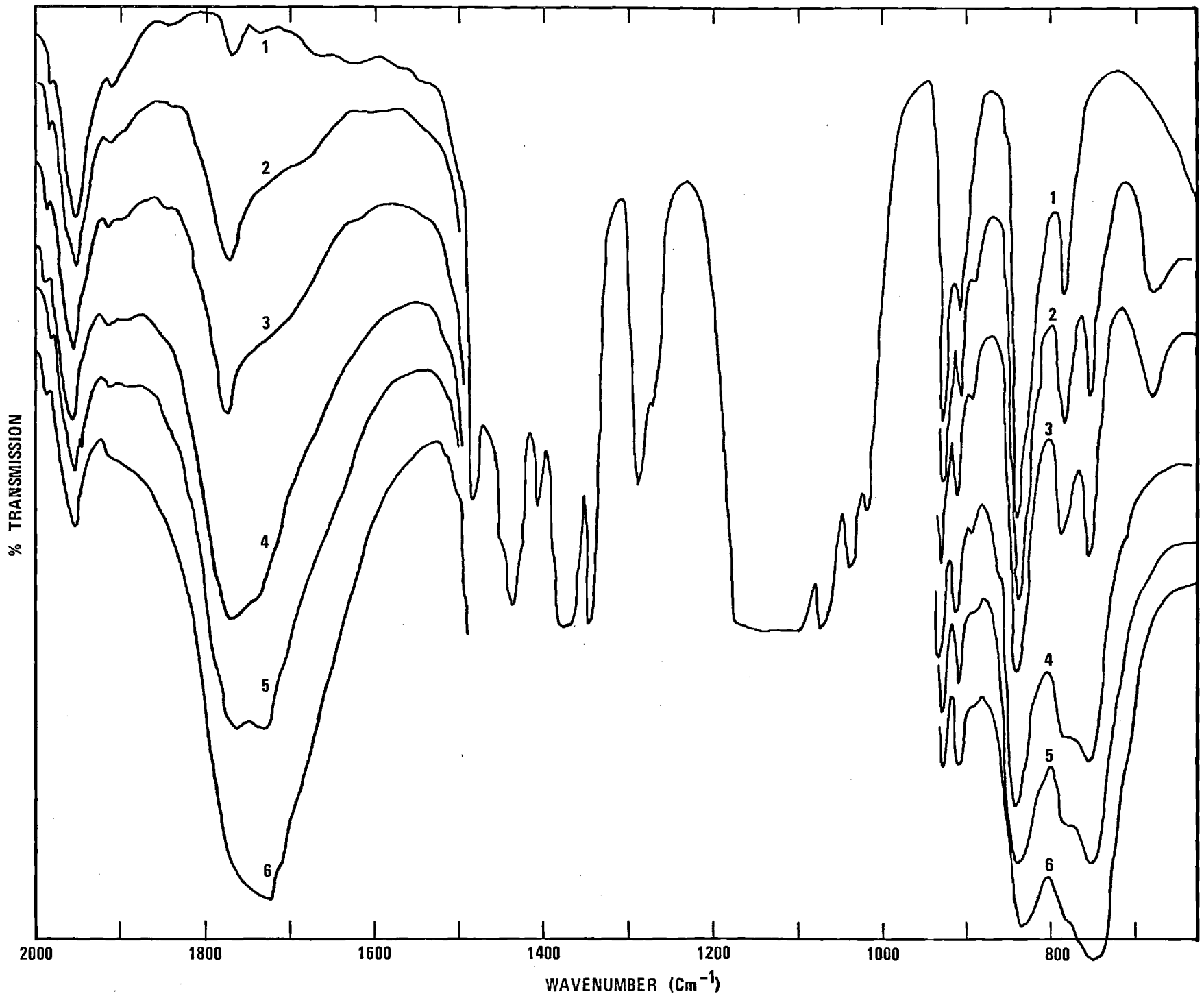

Fig. 1 Reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether. Ratio of $LiAlH_4$:$MgBr_2$ (1) Et_2O (2) 0.5:1.0 (3) 1.0:1.0 (4) 1.5:1.0 (5) 2.0:1.0 (6) 3.0:1.0

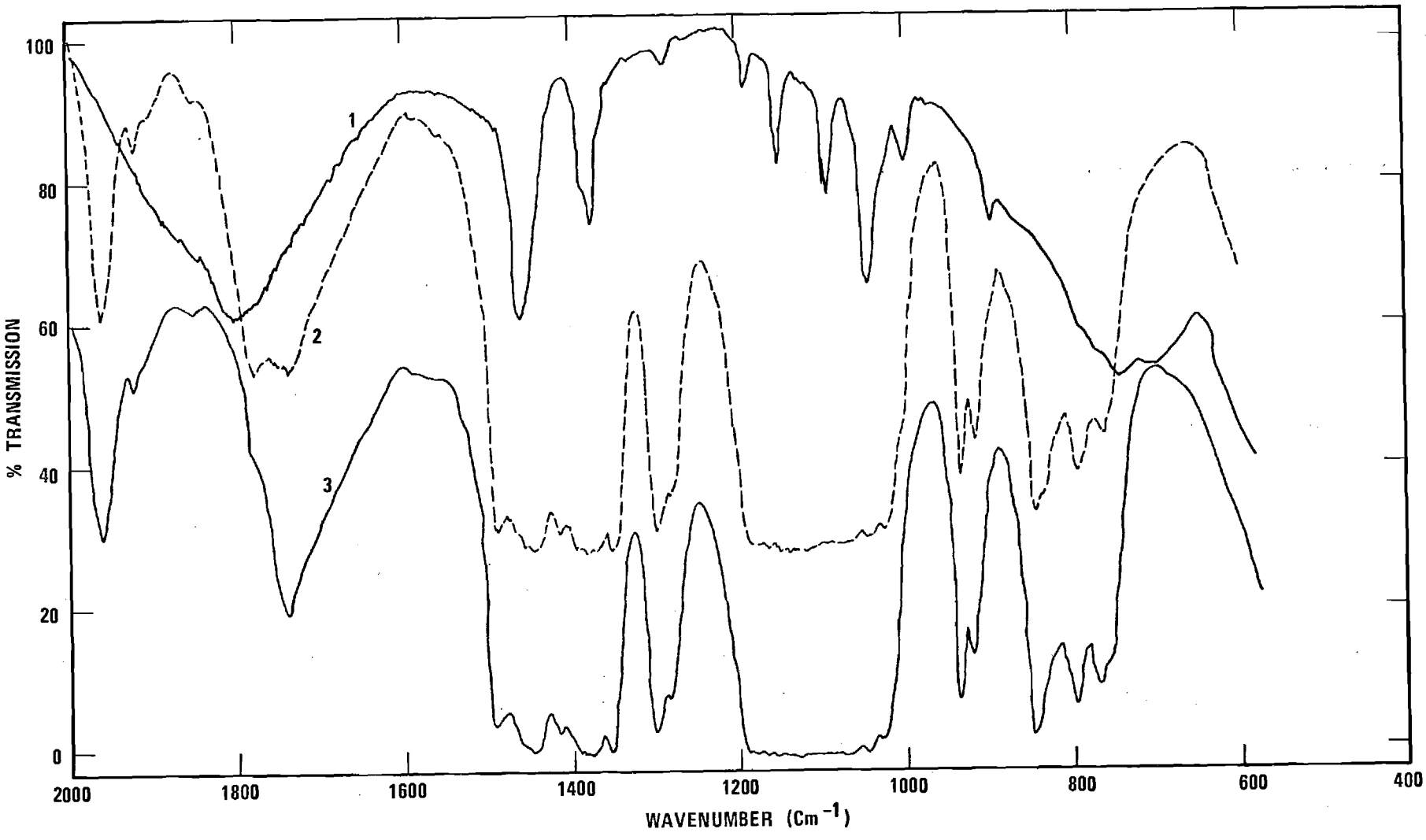

Fig. 2 (1) $Mg(AlH_4)_2 \cdot Et_2O$ in Nujol (2) $Mg(AlH_4)_2$ + LiBr $\xrightarrow{Et_2O}$ reaction product
(3) $LiAlH_4$ in Et_2O.

TABLE I

Infrared Data (Mull Spectra)

$Mg(AlH_4)_2 \cdot 4THF$	$Mg(AlH_4)_2 \cdot 2THF$	$Mg(AlH_4)_2$
1725 S	1785 cm^{-1} S	1855 cm^{-1} S
1025 S	1730 cm^{-1} S	1830 cm^{-1} S
920 W		
875 M		
785 S		
740 S		

$Mg(AlH_4)_2 \cdot Et_2O$	$ClMgAlH_4 \cdot 4THF$	$ClMgAlH_4 \cdot 2THF$	$ClMgAlH_4$
1800 S	1730 S	1775 cm^{-1} S	1850 S
1285 W	1070 W	1030 M	1830 S
1190 W	1030 M	880 M	
1150 M	920 W	810 M	
1090 M	880 M	745 M	
1045 S	745 S		
995 W			
895 W			
740 S			

$BrMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot Et_2O$	$IMgAlH_4 \cdot Et_2O$
1715 S	1830 S	1800 S
1070 W	1290 W	1285 W
1030 M	1260 W	1190 W
915 W	1190 W	1150 W
875 M	1150 W	1090 M
795 S	1090 M	1050 M
745 S	1040 M	900 M
	1000 W	890 W
	900 W	810 S
	750 S	
	720 S	

TABLE II

Infrared Data (Solution Spectra)

$Mg(AlH_4)_2 \cdot 4THF$	$ClMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot 4THF$
1730 M	1715 S	1725 S
800 W	795 M	795 M
750 M	760 M	760 M

$BrMgAlH_4 \cdot Et_2O$
1780 S
760 M

TABLE III

X-ray Powder Patterns. (main lines)

	d	I/Io
$Mg(AlH_4)_2 \cdot 4THF$	8.76	MS
	7.22	VS
	5.84	M
	5.50	M
	4.13	VS
	3.82	M
	3.22	M
$BrMgAlH_4 \cdot 4THF$	11.7	S
	9.71	M
	8.04	S
	7.11	S
	6.19	M
	4.385	VS
	3.86	M
$ClMgAlH_4 \cdot 4THF$	11.5	M
	9.4	M
	8.0	M
	7.0	M
	6.15	M
	5.69	M
	5.24	M
	4.75	M
	4.1	S

	d	I/I
$IMgAlH_4 \cdot Et_2O$	11.6	S
	4.58	S
	3.24	MS
	2.83	MS
$BrMgAlH_4 \cdot Et_2O$	11.6	S
	10.4	M
	8.9	M
	4.6	M
$Mg(AlH_4)_2 Et_2O$		

CONCERNING THE HYDROGENOLYSIS AND PYROLYSIS OF GRIGNARD COMPOUNDS. PREPARATION OF HYDRIDOMAGNESIUM HALIDES

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Abstract

An evaluation of hydrogenolysis and pyrolysis of Grignard compounds as a route to hydridomagnesium halides (HMgX) has been made. Although previous workers report that HMgX compounds (where X = Cl, Br and I) can be prepared by hydrogenolysis, it was found that only HMgCl could be prepared by this method. The products of hydrogenolysis of alkylmagnesium bromides and iodides in diethyl ether solvent were found to be physical mixtures of magnesium hydride and the corresponding magnesium halide due to disproportionation of HMgBr and HMgI in diethyl ether solvent. It was possible to prepare, however, HMgCl, HMgBr and HMgI by the slow and careful pyrolysis of Grignard compounds under vacuum.

Introduction

We have had occasion to investigate and evaluate the preparation of hydridomagnesium halides. The HMgX compounds represent a novel new class of compounds which presumably can function as a selective reducing agent toward organic substrates and as a starting material toward novel complex magnesium hydrides.

The first comprehensive report of the preparation of HMgX compounds was made by Wiberg and Strebel[3] in 1957. These workers reported the preparation

(3) E. Wiberg and P. Strebel, Ann., 607, 9 (1957).

of crystalline soluble compounds [$HMgX \cdot 2(C_2H_5)_2O$ where X = Cl, Br and I] by the reaction of ethyl Grignard reagents and diborane.

$$6\ C_2H_5MgBr + B_2H_6 \rightarrow 6\ HMgBr + 2(C_2H_5)_3B \qquad (1)$$

Later Becker and Ashby[4] found that it was not possible to isolate these

(4) W. E. Becker and E. C. Ashby, Inorg. Chem., 4, 1816 (1965).

compounds over a range of stoichiometries. Instead, chloromagnesium borohydride was obtained.

$$3\ C_3H_5MgCl + 2\ B_2H_6 \rightarrow 3\ ClMgBH_4 + (C_2H_5)_3B \qquad (2)$$

Dymova and Eliseeva[5] reported a second route to HMgX compounds.

$$RCH_2CH_2MgX + H_2 \xrightarrow{\Delta} RCH_2CH_3 + HMgX \qquad (3)$$

(5) T. N. Dymova and N. G. Eliseeva, Russ. J. Inorg. Chem., (English Translation), 8, 8206 (1963).

This method involved the hydrogenolysis of ethyl magnesium halides (where X = Cl, Br and I). They found that all of the HMgX compounds were insoluble in the usual organic solvents and the products contained a non-stoichiometric amount of ether contrary to the results reported by Wiberg and Strebel. They proposed a polymeric structure for the HMgX compounds. At about the same time as the Dymova report, Becker and Ashby[6] reported that hydrogenolysis of

(6) W. E. Becker and E. C. Ashby, J. Org. Chem., 29, 954 (1964).

ether solutions of various Grignard reagents led to formation of MgH_2 and MgX_2 readily and cleanly. The apparent inconsistency between these two latter reports is resolved when it is realized that Becker and Ashby washed all products in their workup procedure with tetrahydrofuran while the Russian workers claim that HMgX compounds disproportionate in tetrahydrofuran.

$$2\ HMgX \xrightarrow{THF} MgH_2 + MgX_2 \qquad (4)$$

A third route reported to produce HMgX compounds involves the pyrolysis of Grignard compounds at ~ 200°. Rice et. al.[7] reported the preparation of

(7) M. J. Rice, Jr. and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ONR-494 (04), (1956).

non-solvated HMgBr by pyrolysis of ethyl magnesium bromide. These workers reported X-ray powder pattern data which were entirely different from that of MgH_2 and $MgBr_2$. The analysis of the product appeared to be unusually good (H:Mg:Br = 1.00:1.00:1.00). Therefore, it was concluded that HMgBr could not be an equimolar mixture of MgH_2 and $MgBr_2$. These workers did report that

extraction of HMgBr with dry ether led to disproportion into MgH_2 and $MgBr_2$ since strong lines for MgH_2 appeared in the X-ray powder pattern of the solid residue. Disproportionation had been observed earlier when HMgCl was stirred in tetrahydrofuran, a solvent in which $MgCl_2$ is soluble.[3]

The controversial points are as follows. If HMgX compounds exist, are they soluble crystalline compounds containing two equivalents of ether ($HMgX \cdot 2Et_2O$) as reported by Wiberg or are these compounds insoluble polymeric solids carrying non-stoichiometric amount of solvent as reported by Dymova[5]? Furthermore, is it possible to prepare HMgX compound by hydrogenolysis of Grignard reagents in ethers such as diethyl ether as reported by Dymova or do HMgX compounds disproportionate in diethyl as reported by Rice?

Here we report our evaluation of hydrogenolysis and pyrolysis of Grignard compounds as routes to HMgX compounds and the stability of these products toward ethers such as diethyl ether and tetrahydrofuran.

Experimental

Material. - Fisher certified reagent grade ethyl bromide, ethyl iodide, i-propyl chloride, i-propyl bromide, i-propyl iodide and i-butyl iodide were distilled over P_2O_5 prior to use. Ethyl chloride was used as received. Mallinkrodt anhydrous ether was further purified by distillation over $LiAlH_4$. All Grignard compounds were prepared using Dow triply sublimed magnesium.

Preparation of Grignard reagents. - Grignard reagents were prepared as described previously.[6] All Grignard reagents were filtered in a dry nitrogen box (equipped with a recirculating system for scrubbing out oxygen, moisture and organic solvents) and stored inside the box. Magnesium was determined by Versene titration and halogens by the Volhard method. In all cases the

magnesium and halogen analyses indicated a magnesium to halogen ratio of 1.0:1.0 to within 2% with exceptions of i-C_3H_7MgBr, i-C_3H_7MgI and i-C_4H_7MgI which contained 2-5% excess magnesium halide.

Hydrogenolysis procedure. - Two different reaction conditions were used based on the previous reports[5,6] (Table I). In one,[5] a 75 or 150 ml. aliquot of a 1 M ether solution of ethyl Grignard reagent was charged into 300 ml. Magne-dash autoclave. The mixture was heated to 100, 125, 150° for 4 to 5 hrs under 1600 to 2400 psi hydrogen. In another procedure,[6] a 50, 75 or 150 ml aliquot of a 2 M ether solution of i-propyl Grignard reagent was heated to 75° for 12 hrs under 1900 to 4700 psi hydrogen. After the reaction mixture had been cooled and vented, it was filtered in the dry box. Both precipitate, after drying under vacuum at 40° for 2 hrs and the filtrate were analyzed for magnesium and halogen as mentioned above. Analysis for hydridic hydrogen, where applicable was accomplished by measuring the gas evolved upon hydrolysis of a weighed sample. The presence of ether was confirmed by hydrolyzing a weighed sample in excess benzene diluent using a minimum amount of 10 vol. % H_2SO_4. The ether released into the benzene was then analyzed. Typical hydrogenolysis experiments are as follows.

Ethylmagnesium chloride. - 75 ml of 1 M ether solution of ethyl magnesium chloride was charged into a 300 ml Magne-Dash autoclave. The mixture was heated to 125° for 4 hrs. under 1400-2000 psi hydrogen. After the reaction mixture had been cooled and vented, it was filtered in a dry box. The white volumenous precipitate was dried under vacuum at 45° for 2 hrs and analyzed. The H:Mg:Cl:ether ratio coupled with X-ray powder pattern data shows that this product is $HMgCl[O(C_2H_5)_2]_x$. The filtrate was found to

contain some (7%) unreacted ethylmagnesium chloride.

Ethylmagnesium bromide. - 150 ml of 1 M ether solution of ethylmagnesium bromide was heated at 150° for 4 hrs under 1800-2200 psi hydrogen. The white compact solid contained H, Mg, Br and ether in the ratio of 1.88:1.00:0.05:0.02. The filtrate showed two layers. Analysis of the lower layer showed a Mg:Br ratio of 1.00:1.64.

i-Propylmagnesium chloride. - 150 ml of 2 M ether solution of i-propylmagnesium chloride was heated at 75° for 12 hrs under 2900-3400 psi hydrogen. Twenty grams (77%) of the white volumenous precipitate contained H:Mg:Cl:ether in the ratio of 0.84:1.00:1.07:0.36. Its X-ray powder pattern is almost exactly the same as that of the hydrogenolysis product of ethylmagnesium chloride. The filtrate contained unreacted (4%) i-propylmagnesium chloride.

i-Propylmagnesium bromide. - 150 ml of 2 M ether solution of i-propylmagnesium bromide was heated at 75° for 17 1/2 hrs under 3400-3800 psi hydrogen. The white compact precipitate contained H:Mg:Br:ether in the ratio of 1.88:1.00:0.07:0.03. The filtrate contained 0.19 g atoms (63%) of Mg and 0.28 g atoms (94%) of Br.

Pyrolysis procedure. - A number of experiments were carried out in order to determine the best combination of reaction temperature and time needed to produce a pure HMgX product. Typical results are shown in Table 2. A typical procedure for pyrolysis of Grignard reagents follows.

Grignard reagents in ether were charged into a 200 ml round bottom flask containing a large "egg shape stirring bar. The ether was removed under vacuum at 50°C. The Grignard solution gradually became viscous during the

ether solvent removal process until finally the stirrer could not move. At this stage, the stirrer was made to move by occasional shaking of the flask while the temperature was increased to the reaction temperature. Pyrolytic reactions of ethyl- and i-propylmagnesium bromide and i-propylmagnesium chloride were carried out in this way.

In another procedure, the ether was removed under vacuum at 50° until the stirring bar stopped moving. Then nujol was added and the mixture was heated to 90° for a prolonged time (120 hrs) to insure complete removal of solvated ether. Then the temperature was raised gradually to the point where pyrolysis was carried out over a period of 1 hr. i-Butylmagnesium iodide was pyrolyzed in this way. A white product instead of a gray one was obtained.

Disproportionation reactions. - 2.684 g of HMgCl (H:Mg:Cl:ether = 0.84:1.00:1.07:0.36) prepared by the hydrogenolysis of EtMgCl in diethyl ether was stirred in 50 ml of dry THF for 3 minutes. The mixture was filtered quickly and 0.42 g of the white solid was obtained. The solid product and the filtrate were analyzed. The solid contained H:Mg:Cl in the ratio of 1.77:1.00:0.10 and its X-ray powder pattern showed lines only for MgH_2. The filtrate contained 99% and 62% of the original amount of Cl and Mg, respectively. Experiments using HMgCl, HMgBr and HMgI prepared from pyrolysis reactions gave similar results which are shown in Table 3. The X-ray powder pattern of the residue from THF treatment of the HMgCl produced from a pyrolysis experiment showed strong lines for the original HMgCl and medium strong lines for MgH_2.

Results and Discussion

Our evaluation of the reaction of ethyl Grignard compounds with diborane as a route to HMgX compounds was reported earlier.[4] We were not able to

prepare HMgX compounds by this method under any conditions including the exact conditions stated by Wiberg and Strebel in their earlier report. It was clearly demonstrated that the products of this reaction in tetrahydrofuran under a variety of conditions, are the halogenomagnesium borohydride ($XMgBH_4$) and triethylborane.

The two other methods for the preparation of HMgX compounds which have been reported involve hydrogenolysis and pyrolysis of Grignard compounds. As a starting material for hydrogenolysis and pyrolysis reactions, ethyl, i-propyl and i-butyl magnesium halides were chosen. i-Propyl compounds were chosen because earlier we had shown that i-propyl magnesium chloride reacts with hydrogen at a faster rate than any other Grignard compounds investigated at the time. Thus lower reaction temperatures could be used to effect hydrogenolysis of the i-propyl Grignard reagent which presumably would lead to a purer product. i-Butyl compounds were investigated since tri-i-butylaluminum is known to undergo hydrogenolysis and pyrolysis readily compared to other aluminum alkyls. The ethyl Grignard compounds were investigated because previous workers used these compounds for both hydrogenolysis and pyrolysis studies and it was considered necessary to repeat this work.

Hydrogenolysis of both ethyl and i-propyl magnesium chloride produced $HMgCl\cdot(O(C_2H_5)_2)_n$ which contained hydridic hydrogen, magnesium, chlorine and ether in the approximate ratio of 1:1:1:n (where $n < 1$). The hydrogen content was always slightly low and the chlorine content slightly high (Table 1). The X-ray powder pattern of the product from both the ethyl- and i-propylmagnesium chloride showed similar clear lines which could not be found in the diffraction

pattern of MgH_2 and $MgCl_2$. Therefore it was concluded that the product could not be an equimolar mixture of MgH_2 and $MgCl_2$. Contrary to the earlier report by Dymova and Eliseeva[5] we were not able to obtain $HMgX\cdot[O(C_2H_5)_2]_n$ (where X = Br and I) by hydrogenolysis of Grignard compounds in diethyl ether. Twelve hydrogenolysis experiments were carried out in which several Grignard compounds were allowed to react under a variety of conditions, (varying the temperature, pressure and concentration), including those specified by the Russian workers. Under all conditions, when the Grignard compound was a bromide or iodide, a white solid was formed which was shown by both elemental and X-ray powder analyses to be predominantly MgH_2. The filtrate contained almost all of the initial halide (Table 1). It seems clear that the HMgX compounds disproportionate readily in diethyl ether when X = Br and I, but not Cl.

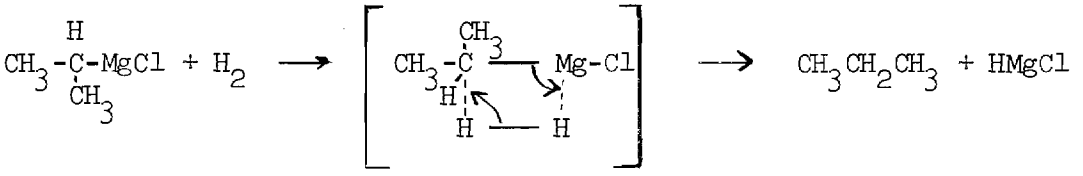
$$2\ HMgX \rightleftarrows MgH_2 + MgX_2 \qquad (4)$$

These observations are not difficult to rationalize. HMgCl would be expected to be very insoluble in diethyl ether since both MgH_2 and $MgCl_2$ are known to be very insoluble in this solvent. Thus HMgCl cannot readily disproportionate since it immediately precipitates from solution as it is formed. On the other hand, $MgBr_2$ and MgI_2 are quite soluble in diethyl ether, thus HMgBr and HMgI should have greater solubility in diethyl ether than does HMgCl. In this way equilibrium (4) is more favorably displaced to the right as $MgBr_2$ or MgI_2 solubilizes and MgH_2 precipitates.

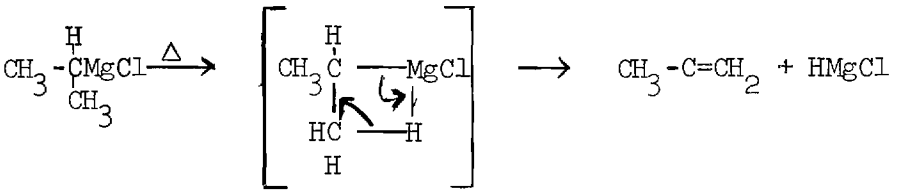
Although it was not possible to prepare HMgBr or HMgI by hydrogenolysis of Grignard compounds in diethyl or tetrahydrofuran,[6] it was possible to

prepare these compounds by pyrolysis of Grignard compounds. We were not able to prepare as pure a product (HMgBr) as claimed by Rice,[7] however it was possible to prepare reasonably pure HMgBr from i-propylmagnesium bromide (Table 2). An X-ray powder pattern of the product contained almost all of the lines reported for the pyrolytic product of C_2H_5MgBr reported by Rice.[5] Also this powder pattern was quite different from that produced by a physical mixture of MgH_2 and $MgBr_2$. Essentially similar results were obtained in the case of HMgI.

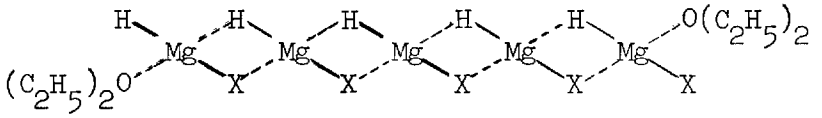
HMgCl was obtained by pyrolysis of i-propyl magnesium chloride. The X-ray powder pattern of this product had clear lines but was different not only from those of MgH_2 and $MgCl_2$ but also from that of the HMgCl prepared by hydrogenolysis of i-propylmagnesium chloride. The reason for this is not clear, however the difference might be due to the different amount of solvated ether present in the two products. Also it is possible that since the products are prepared under considerably different conditions that two different crystalline modifications are formed. In one case (hydrogenolysis) a product is formed in diethyl ether solution presumably via a four-center transition state.



On the other hand, pyrolysis takes place not in solution but in the solid state with no solvated ether present. Presumably this reaction proceeds by an olefin elimination mechanism.



When $HMgCl \cdot [O(C_2H_5)_2]_n$ prepared by either hydrogenolysis or pyrolysis of Grignard compounds was extracted with THF, the insoluble solid portion changed its composition considerably and became rich in hydrogen content whereas the THF extractant became rich in $MgCl_2$ (Table 3). Similarly $HMgX \cdot [O(C_2H_5)_2]_n$ (X = Br and I) prepared by pyrolysis of alkylmagnesium bromides and iodides, was converted into magnesium hydride in the solid state and magnesium halides in solution by ether extraction. These disproportionation reactions took place in a matter of minutes. These observations coupled with the insolubility of these compounds in the usual organic solvents are consistent with the suggestion by Dymova and Eliseeva[5] that HMgX compounds are polymeric in the solid state.



This type of structure accounts for both the non-stoichiometry of the solvated ether and the facile disproportionation reaction.

Infrared spectra of HMgCl produced by hydrogenolysis of i-propylmagnesium chloride as well as HMgCl and HMgBr produced by pyrolysis reactions, were not well defined. The spectra showed two very broad bands centered around 1200 cm^{-1} and 650 cm^{-1}. On the other hand, the infrared spectrum of HMgI produced by pyrolysis showed two well-resolved characteristic bands centered at 950 cm^{-1} with the half height width of 150 cm^{-1} and at 625 cm^{-1}

with the half height width of 65 cm^{-1}. Interestingly all of the products from pyrolysis of n-butyl-, i-butyl- and ethylmagnesium iodide showed similar bands growing as the pyrolysis reaction proceeded.

In conclusion, HMgCl can be prepared both by hydrogenolysis in ether and pyrolysis of Grignard compounds. However, HMgBr and HMgI can be prepared only by pyrolysis of Grignard compounds. The polymeric structure for HMgX compounds (containing a non-stoichiometric amount of ether) suggested earlier is consistent with the observations made in this study.

Hydridomagnesium halides are subject to rapid disproportionation in the presence of ether solvents into which the corresponding magnesium halide is appreciably soluble.

Acknowledgment. - The authors are indebted to the Office of Naval Research Contract authority No. NR 093-050112-5-67---429 under ONR Contract No. N 00014-67-A-0159-0005 for support of this work.

TABLE I

Hydrogenolysis of Grignard Reagents

Ex. No.	Experimental Conditions: RMgX	Concentration (mole/l)	Pressure (p.s.i.g.)	Reaction Time (hr)	Temperature (°C)	Analysis of Product (Atomic Ratio): H	Mg	X	ether	Halogen Recovery from filtrate (%)
1	C_2H_5MgCl	1.0	1400-2000	4	125	0.83	1.00	1.03	0.26	7
2*	C_2H_5MgBr	1.7	2100-2800	3 1/2	150	0.73	1.00	1.01	0.45	
3	C_2H_5MgBr	1.0	1900-2200	4	150	1.90	1.00	0.07	0.03	
4	C_2H_5MgBr	1.0	1800-2000	4	150	1.88	1.00	0.05	0.02	
5	C_2H_5MgBr	0.5	1600-2000	4	150	1.94	1.00	0.06	0.00	
6	C_2H_5MgBr	1.0	1550-1750	5	125	1.78	1.00	0.10	0.03	
7	C_2H_5MgBr	1.0	2000	16	125	2.02	1.00	0.05	0.07	
8	C_2H_5MgBr	1.0	4000-4500	4	100-125	1.90	1.00	0.07	0.07	
9	C_2H_5MgBr	3.9	1500-3000	5	100	1.62	1.00	0.30	0.15	
10	C_2H_5MgI	1.0	2250	4	125	1.74	1.00	0.13	0.16	88
11	C_2H_5MgI	1.0	2000-2100	4	100	1.30	1.00	0.10	0.22	93
12	$i\text{-}C_3H_7MgCl$	2.0	3600-4700	12	75	0.86	1.00	1.04	0.29	
13	$i\text{-}C_3H_7MgCl$	2.0	2900-3400	12	75	0.84	1.00	1.07	0.36	4
14	$i\text{-}C_3H_7MgCl$	2.0	1900	4	75	0.77	1.00	1.09	0.97	
15	$i\text{-}C_3H_7MgCl$	2.0	1900-2000	4	75	0.72	1.00	1.19	0.68	
16	$i\text{-}C_3H_7MgBr$	2.0	2000	3.5	75	1.89	1.00	0.14	0.12	
17	$i\text{-}C_3H_7MgBr$	2.0	3400-3900	17.5	75	1.88	1.00	0.07	0.03	94
18	$i\text{-}C_3H_7MgI$	1.0	4500-4700	12	75	1.71	1.00	0.11	0.10	98

* Almost all of ether was gone. No X-ray powder pattern was obtained.

TABLE 2

Pyrolysis of Grignard Reagents

Ex. No.	Experimental Conditions: RMgX	Temperature (°C)	Reaction Time (hr)	Pressure (mmHg)	Atomic-molar Ratio: H	Mg	X	ether*
1	C_2H_5MgBr	195	22	3	0.56	1.00	0.99	0.26
2		195	18	1	0.51	1.00	0.99	0.31
3		195	6	3	0.39	1.00	1.00	0.34
4		150	5	3	0.53	1.00	0.98	0.44
5	$i\text{-}C_3H_7MgCl$	140	4	3	0.74	1.00	1.02	0.15
6		140	2.5	4	0.74	1.00	1.08	0.05
7		140	1	2	0.71	1.00	1.12	0.01
8		140	0.5	4	0.67	1.00	1.05	0.12
9		130	17	3	0.69	1.00	0.95	0.01
10		130	10	5	0.54	1.00	1.20	0.13
11		130	6	3	0.83	1.00	1.07	0.03
12		130	6	5	0.79	1.00	1.04	0.04
13		130	4	3	0.80	1.00	1.03	0.08
14		130	2	2	0.61	1.00	1.09	0.31
15		130	1	4	0.51	1.00	1.05	0.33
16		110	72	3	0.84	1.00	1.05	0.33
17		110	16	5	0.78	1.00	1.04	0.13
18		110	5	5	0.73	1.00	0.99	0.17
19	$i\text{-}C_3H_7MgBr$	160	5.5	1	0.83	1.00	1.07	0.04
20		140	6	1	0.81	1.00	1.09	0.09
21		130	6	3	0.72	1.00	1.08	0.21
22		120	6	1	0.56	1.00	1.07	0.34
23		110	24	3	0.65	1.00	1.07	0.26
24	i-BuMgI	150-160	1 1/3	0.5	0.49	1.00	1.12	

TABLE 2 (continued)

Pyrolysis of Grignard Reagents

Ex. No.	Experimental Conditions: RMgX	Temperature (°C)	Reaction Time (hr)	Pressure (mmHg)	Atomic-molar Ratio: H	Mg	X	ether*
25		150-160	2 1/3	0.5	0.56	1.00	1.20	
26		160-170	1	1	0.75	1.00	1.08	0.162
27		170	1	1	0.78	1.00	1.06	0.802
28		170	2	1	0.74	1.00	1.06	
29		180	1	1	0.76	1.00	1.05	0.245
30		205	1	1	0.70	1.00	1.06	1.34

* Ether by difference.

TABLE 3

The Results of Disproportionation Reaction

Compound	Solvent	Atomic ratio of original compound			Analysis of Residue (Atomic ratio)			Analysis of solution (%)	
		H	Mg	X	H	Mg	X	Mg	X
Hydrogenolysis HMgCl[a]	THF	0.84	1.00	1.07	1.77	1.00	0.10	62	99
Pyrolysis HMgCl[b]	THF	0.79	1.00	1.09	1.02	1.00	0.73	49	60
Pyrolysis HMgBr[a]	ether	0.83	1.00	1.07	1.68	1.00	0.13	43	78
Pyrolysis HMgI	ether	0.73	1.00	1.09	1.43	1.00	0.07		
Pyrolysis HMgI	THF	0.73	1.00	1.09	0.83	1.00	1.17		

a X-ray powder pattern of these cases show lines only for MgH_2

b X-ray powder pattern of these cases show strong lines for original compound and medium strong lines for MgH_2

TABLE 4

X-ray Powder Pattern d-spacing Data

	$MgCl_2 \cdot Et_2$	$MgBr_2 \cdot OEt_2$	$MgI_2 \cdot 2OEt_2$	MgH_2 (hydrogenolysis)	HMgCl (hydrogenolysis)	HMgCl (pyrolysis)	HMgBr (pyrolysis)	HMgI (pyrolysis)
1	10.6 v.s.	8.0 S	8.0 M	3.19 S	12.5 M	8.3 VW	6.3 M	3.60 VW 3.42 W
2	9.5 VW	7.3 S	6.90 M	2.51 S	9.3 S	7.5 M	4.5 VW	3.18 S
3	7.8 W	5.7 VW	6.10 W	2.25 M	7.2 M	6.7 VW	3.32 W	2.48 M
4	7.0 VW	5.3 W	5.70 VW	1.68 S	6.3 VW	6.0 S	3.15 M	2.08 M
5	6.3 W	4.40VW	5.20 M	1.59 W	5.5 VW	3.6 VW	2.95 S	1.93 M
6	6.0 W	3.95 VW	4.30 W	1.51 VW	4.75 VW	3.2 VW	2.73 W	1.78 M
7	5.6 W	3.55 S(b)	3.94 VW	1.43 W	3.14 W 2.76 VW	3.1 VW	2.50 VW	1.74 W
8	2.9 W	3.42 VW	3.88 WW	1.36 W	2.50 VW	2.98 S	2.33 VW	1.72 W
9	2.5 W	3.24 M	3.80 W	1.35 W	2.35 VW	2.79 VW	2.28 M	1.60 VW
10	2.26 W	3.18 VW	3.66 W	1.25 W	2.13 VW	2.60 S	1.92 S	1.56 WW
11	1.80 W	2.98 M	3.43 M (b)	1.16 W	1.82 VW	2.52 W	1.84 VW	1.42 VW
12		2.86 VW	3.31 W	1.13 W		2.43 VW	1.78 W	1.34 W
13		2.75 VW	3.20 W			2.27 VW	1.68 VW	1.33 W
14		2.62 VW	3.05 W			2.02 VW	1.64 M	1.29 VW
15		2.51 W(b)	2.86 VW			1.83 S	1.61 W	1.27 VW
16		2.39 W(b)	2.75 VW			1.75 W	1.57 W	1.20 WW
17		2.24 VW	2.64 VW			1.69 W	1.23 W	1.17 VW
18		2.13 VW	2.48 W			1.56 W	1.22 W	1.13 VW
19		2.07 VW	2.38 VW			1.49 W		1.10 WW
20		1.90 W	2.33 VW					
21		1.84 VW	2.26 VW					
22		1.73 VW	2.20 VW					
23		1.61 VW	2.13 VW					
24		1.58 VW	2.09 VW					
25			2.06 VW					
26			1.83 VW					

TABLE 5

Analyses of Grignard Solutions

Grignard	Mg	X	Ratio Mg:X	% MgX_2
EtMgBr (1)	1.74 M	1.70 M	1.000:0.977	2%
i-PrMgCl (1)	0.361	0.365	1.000:1.011	1%
i-PrMgCl (2)	2.55	2.61	1.000:1.024	2%
EtMgBr (2)	3.88	3.85	1.000:0.992	1%
EtMgBr (3)	3.64	3.65	1.000:0.997	1%
i-PrMgCl (3)	2.48	2.50	1.000:1.000	0%
i-PrMgCl (4)	1.99	2.09	1.000:1.050	5%
i-PrMgBr (1)	1.92	2.04	1.000:1.062	6%
EtMgCl (1)	3.58	3.60	1.000:1.009	1%
EtMgI (1)	3.54	3.44	1.000:0.972	2%
i-PrMgI (1)	1.07	1.26	1.000:1.178	18%
i-PrMgI (2)	1.001	1.125	1.000:1.118	12%
i-PrMgI (3)	0.894	1.07	1.000:1.200	20%
i-PrMgI (4)	0.206	0.251	1.000:1.218	21%
i-PrMgCl (5)	1.714	1.724	1.000:1.007	1%
i-PrMgBr (2)	0.812	0.823	1.000:1.014	1%
i-BuMgI (4)	0.594	0.029	1.000:1.059	6%

Experimental Number refers to Table 1 and Table 2

EtMgBr reagents had Mg:Br ratio of $1.0:1.0 \pm 0.02$.

All of pyrolytic and hydrogenolytic reactions of i-PrMgBr was done by i-PrMgBr (1).

Hydrogenolysis of i-PrMgCl were done using i-PrMgCl (4).

Pyrolyses of i-PrMgCl were done using i-PrMgCl (3).

Pyrolyses of i-PrMgCl were done using i-PrMgCl (2).

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Georgia Institute of Technology	Non-Classified
	2b. GROUP

3. REPORT TITLE

Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Annual Report (March 1, 1968 - February 28, 1969)

5. AUTHOR(S) *(First name, middle initial, last name)*

E. C. Ashby

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 15, 1969	54	29

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
N00014-67-A-0159-0005	
b. PROJECT NO. NA	1
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

Efforts during the report period have centered about three projects. All three projects are nearly complete and carry the following titles: (1) "Concerning the Reaction of Lithium Aluminum Hydride with Diethylmagnesium in Diethyl Ether," (2) "Concerning the Preparation of Magnesium Aluminum Hydride. A Study of the Reactions of Lithium and Sodium Aluminum Hydride with Magnesium Halides in Ether Solvents" and (3) "Concerning the Hydrogenolysis and Pyrolysis of Grignard Compounds. Preparation of Hydridomagnesium Halides." Each project has as its objective the exploration of fundamental chemistry related to simple and complex metal hydrides. In each project fundamental prior disclosures by previous workers have been corrected and new findings reported. The initial objective of establishing the nature of these fundamental reactions related to hydride chemistry is nearly complete. Thus the attempted preparation of novel metal hydrides can proceed shortly.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Complex Metal Hydrides						
High Energy Fuels						

DD FORM 1 NOV 65 1473 (BACK)

S/N 0101-807-6821

Non-Classified

Security Classification

A-31409

Annual Report

to the

Office of Naval Research

"Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors."

E. C. Ashby, Principal Investigator

Georgia Institute of Technology, Atlanta, Georgia 30332

March 1, 1971 - February 29, 1972

This Research was Sponsored by the Office of Naval Research under Contract No. N00014-67-A-0519-005AD and ONR Contract Authority No. NR 093-050/7-11-69(473)

Table of Contents

Appendix

Attached Publications

Report Abstract

The fourth annual report concerning the preparation and structure elucidation of simple and complex metal hydrides of the main group elements describes significant progress in this area. This report is divided into three categories. The first category describes work in progress (Pages 1 - 70), the second category describes work completed since the last report period (Pages 71 - 115) and the third category lists the papers published in the journals since the last report period.

In the first category concerning work in progress, five studies are reported. The first study is concerned with the direct synthesis of polyiminoalanes from aluminum, hydrogen and primary amines. The study shows feasibility in that N-t-butyliminoalane was prepared in good yield by this method. This class of compounds represents a very important class of polymerization catalysts. N-n-butyliminoalane will polymerize isoprene to isotactic poly-cis-1,4-isoprene of high crystallinity. In addition, it should be an excellent candidate as a high energy binder. Because of the low cost to make such a compound, patent coverage is suggested. The second, third, and fourth studies describe successful methods for the preparation of complex metal hydrides of magnesium, zinc, and copper (e.g., $LiMgH_3$, Li_2ZnH_4, and $LiCuH_2$). These compounds represent complex metal hydrides of Groups IB, IIA, and IIB which were heretofore unknown. The method of preparation is unique and the synthesis of such compounds can be considered a major achievement in metal hydride chemistry. The fifth and final study in progress describes the construction of high vacuum DTA-TGA instrumentation capable of determining the composition of gases evolved on decomposition of a hydride. It took about four months

to build and perfect this instrumentation, however, the information we are obtaining from this instrumentation was well worth the effort.

In the second category concerning work completed since the last report period (but which is not yet published), two studies are reported. In the first study the controversy surrounding the existence of $HMgAlH_4$ and $HMgBH_4$ has been settled to our satisfaction. These compounds exist only as physical mixtures of MgH_2 and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$. In the second study a detailed evaluation of the reaction of $LiAlH_4$ and $NaAlH_4$ with organomagnesium compounds (R_2Mg and RMgX) has been made. The previously reported reaction products ($RMgAlH_4$, etc.) have been shown not to exist [the product is actually $HMgAlH_3R$ or $MgH_2 + Mg(AlH_3R)_2$) depending on the nature of the R group]. The complete details of the reaction were determined in order to understand this fundamental reaction.

In the third category involving work published since the last report period, six studies are reported.

Papers Published Since the Last Report

1. R. A. Kovar and E. C. Ashby, "Aminoalanes. Direct Synthesis from Aluminum, Hydrogen and Secondary Amines. Structure and Stability Elucidation by Nuclear Magnetic Resonance, Infrared Spectra and Differential Thermal and Thermal Gravimetric Analysis," Inorg. Chem., 10, 893 (1971).

2. R. A. Kovar, R. Culbertson, and E. C. Ashby, "A Convenient Synthesis of Aminoboranes," Inorg. Chem., 10, 900 (1971).

3. E. C. Ashby and R. A. Kovar, "Synthesis of N-Trialkylborazines from Phenyl Borate, Aluminum, Hydrogen and Primary Amines," Inorg. Chem., 10, 1524 (1971).

4. R. G. Beach and E. C. Ashby, "Synthesis and Characterization of Dialkyl (Aryl)aminomagnesium Hydrides and Alkoxy(Aryloxy)magnesium Hydrides," Inorg. Chem., 10, 906 (1971).

5. R. G. Beach and E. C. Ashby, "The Reaction of Lithium Aluminum Hydride with Secondary Amines in Diethyl Ether," Inorg. Chem., 10, 1888 (1971).

6. E. C. Ashby and R. G. Beach, "Preparation of New Complex Metal Hydrides. Potassium Tetrahydrozincate and Sodium Tetrahydrozincate," Inorg. Chem., 10, 2486 (1971).

The Direct Synthesis of Polyiminoalanes

E. C. Ashby and T. F. Korenowski

Abstract

The feasibility of preparing polyiminoalanes by the direct reaction of a primary amine with aluminum and hydrogen has been demonstrated.

Introduction

Polyiminoalanes are reported to be excellent co-catalysts for polymerizing ethylene and isoprene,[1] however, these compounds are either inconvenient or expensive to prepare by known procedures.[2,3,4,5]

(1) S. A. Snam, U. S. Pat. 3,242,156 (1966); Snam and Progetti, Fr. Pat. 1,465,859 (1966); Snam and Progetti, Belg. Pat. 675,279 (1965).

(2) E. Wiberg and A. May, Z. Naturforsch., 10b, 232 (1955).
(3) R. Ehrlich, A. R. Young, II, B. M. Lichstein, D. D. Perry, Inorg. Chem., 3, 628 (1964).
(4) R. F. Land, Makrom. Chemie, 83, 274 (1965).
(5) A. Mazzei, S. Cucinella, and W. Marconi, Makrom. Chemie, 122, 168 (1969).

Recently, we have demonstrated that aminoalanes can be prepared by a convenient and economical synthesis involving direct reaction of aluminum, hydrogen, and secondary amines.[6] These results suggested to us that polyiminoalanes could be prepared by a similar route.

(6) R. A. Kovar and E. C. Ashby, Inorg. Chem., 10, 893 (1971).

Therefore, we have begun to study a direct synthesis of poly-iminoalanes and would now like to report the preliminary results of this investigation.

We have recently prepared poly(N-t-butyliminoalane) in reasonable yield by reaction of aluminum, hydrogen, and t-butylamine at moderate temperature and pressure.

$$t\text{-}C_4H_9NH_2 + n\ Al \xrightarrow[\text{benzene}]{H_2,\Delta,P} (t\text{-}C_4H_9NAlH)_n + n/2\ H_2 \qquad (1)$$

Presumably the reaction occurs by initial formation of an unstable t-butylaminealane complex followed by loss of hydrogen to form the imino-alane. A similar scheme has been envisioned for the direct synthesis of aminoalanes.[6]

$$R_2\overset{H}{N}AlH_3 \xrightarrow{-H_2} RN\overset{H}{-}AlH_2 \xrightarrow{-H_2} [RNAlH]_n \qquad (2)$$

To prepare poly(N-t-butyliminoalane), 3.0 g (0.11 mm) activated aluminum powder, 10.0 ml (0.96 mm) t-butylamine, and 100 ml benzene were heated to 120° for 8 hours under 4000 psig hydrogen pressure. The reaction solution was then cooled to room temperature and filtered to remove unreacted aluminum. Solvent was removed under vacuum from a measured aliquot of the filtrate to yield the solid, white poly(N-t-butyliminoalane). Analysis of the solid revealed aluminum, hydrolyzable hydrogen, and nitrogen to be present in nearly equal molar quantities (Al:N:H, 1.00:0.95:0.96). Analysis for hydrolyzable hydrogen was by gas evolution and aluminum by EDTA titration. Nitrogen was determined by standard acid titration of the solution obtained on hydrolysis after separation of aluminum hydroxide. The yield, based on soluble aluminum,

was determined to be 72% of the theoretical value.

The infrared spectrum of the solid in a nujol mull exhibited a strong aluminum-hydrogen stretching absorption at 1852 cm^{-1} which compared favorably with ν Al-H values reported for similar polyiminoalanes.[4,5]

The thermal behavior of poly(N-t-butyliminoalane) was studied by simultaneous differential thermal and thermal gravimetric analysis using a Mettler Thermoanalyzer II. When subjected to DTA-TGA analysis under a steady flow of argon, a tared sample exhibited gradual weight loss over the temperature range of 80° to 300° with no identifiable endothermic or exothermic effects. Total weight loss was 72.4% of the initial, which was consistent with the formulation $(t\text{-}C_4H_9NAlH)_n$.

An initial attempt to demonstrate the general applicability of reaction (1) was not successful. When n-butylamine was substituted for t-butylamine in reaction (1) either the starting materials were recovered unchanged or unknown materials were produced which contained variable ratios of aluminum and nitrogen (Al:N, 1.00:0.95-1.33) and only trace quantities of hydrolyzable hydrogen.

At this early stage of investigation, our information is yet too limited to make any meaningful interpretation of the n-butylamine system and it would be premature to draw any conclusions as to the ultimate potential of the direct synthesis of polyiminoalanes from aluminum, hydrogen and primary amines.

It remains clear, however, that we have succeeded in preparing a polyiminoalane by methods heretofore unknown. We expect further study of this reaction with n-butylamine and other primary amines which will

enable us to define the scope and value of this synthesis as a convenient and economical method for the preparation of polyiminoalanes.

Synthesis of Complex Metal Hydrides of Magnesium

Suresh C. Srivastava and E. C. Ashby

Abstract

A series of complex metal hydrides of magnesium of the general composition $M_xMg_yR_zH_{(X + 2y)-z}$ has been prepared and characterized, where M = Li or Na and R = CH_3 or s-C_4H_9. The 1:1 complex of potassium hydride with di-s-butylmagnesium reacts with lithium bromide in diethyl ether to form the soluble $LiMg_2(s\text{-}C_4H_9)_4H$. Reaction of this compound with lithium aluminum hydride in diethyl ether produces insoluble $LiMg_2H_5$. The reaction of $KMg(s\text{-}C_4H_9)_2H$ with $LiAlH_4$ in diethyl ether produces an insoluble solid with the composition $KMgH_3$ + 2 $LiMgH_3$. In tetrahydrofuran the same reaction gives the soluble products $KAlH_4$ and $LiMg(s\text{-}C_4H_9)_2H$, however, benzene precipitates $KAlH_4$ from the mixture. A reaction of sodium iodide with $KMg(s\text{-}C_4H_9)_2H$ precipitates insoluble KI leaving $NaMg(s\text{-}C_4H_9)_2H$ in solution. Upon reacting $NaMg(s\text{-}C_4H_9)_2H$ with $LiAlH_4$ in tetrahydrofuran, insoluble $NaMgH_3$ is produced. There is some evidence for the formation of $LiMgH_3$ from a reaction of $LiMg(s\text{-}C_4H_9)_3$ with $LiAlH_4$ in diethyl ether. Reactions of $Li_2Mg(CH_3)_4$ and $Li_3Mg(CH_3)_5$ with lithium aluminum hydride in diethyl ether produce the white insoluble solids, Li_2MgH_4 and Li_3MgH_5, respectively.

Introduction

During the past several years efforts have been directed towards preparing complex metal hydrides of magnesium with little or no success.[1,2]

(1) J. Tanaka and R. Westgate, 157th National ACS Meeting, 1969, Paper No. 155, Inorganic Chemistry Section.

(2) G. E. Coates and J. A. Heslop, J. Chem. Soc., (A), 574 (1968).

The importance of the analogous aluminum and boron hydrides, e.g., $LiAlH_4$, $NaBH_4$, etc., in both organic and inorganic chemistry cannot be overemphasized.[3] Complex metal hydrides of alkali metals with magnesium, although

(3) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, New York, 1956.

highly sought after, were not known until recently when, for the first time, a successful synthesis of $KMgH_3$ was achieved in these laboratories. The compound was prepared by the hydrogenolysis of $KMg(s\text{-}C_4H_9)_2H$ in benzene solution.[4,5] The preparation of $NaMg_2H_5$ and the existence of $NaMgH_3$ was

(4) E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 21, 29 (1970).

(5) E. C. Ashby, R. Kovar and R. C. Arnott, J. Amer. Chem. Soc., 92, 2182 (1970).

also suggested through a similar reaction.[6]

(6) R. C. Arnott, Ph.D. Thesis, Georgia Institute of Technology, 1971.

The unique solubility of the alkali metal hydride-di-secondary-

butylmagnesium complexes in hydrocarbon media has been used with advantage, thus eliminating the need for hydrogenolysis in more basic ether solvents which often results in extensive cleavage products. Moreover, s-butyl groups bonded to relatively electropositive metals undergo hydrogenolysis under much milder conditions. Using this same reaction path, we have recently reported the preparation of compounds like NR_4MgH_3 (R = trioctylpropyl) and $LiMgH_2(OC_4H_9)$ and other R-H compounds.[7]

(7) "Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors," ONR Annual Progress Report, Contract No. N00014-67-A-0519-005AD, pp. 37-51 (1971).

Thus, until now the only workable method for converting the Mg-R compounds to Mg-H compounds with limited success has been the high pressure hydrogenation of M-R compounds in hydrocarbon solvents with R=s-butyl. More recently, we have discovered that this operation can be performed by reacting the M-R compounds with lithium aluminum hydride in ether solvents at room or lower temperatures. The present paper describes several such reactions and the results obtained so far.

Experimental Section

Apparatus. All operations were performed under a nitrogen atmosphere using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen (MnO) and moisture (Dry Ice-acetone traps) or on the bench top using Schlenk tube techniques.[8] All glassware

(8) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, New York, 1969.

was flash flamed and flushed with dry nitrogen prior to use.

Infrared spectra were obtained using a Perkin-Elmer 621 grating spectrophotometer. Cesium iodide windows were used. Solid spectra were recorded as mulls in nujol which had been dried over sodium wire and stored in a nitrogen filled glove box.

X-ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered CuK_{α} radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hrs. D-spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Hydrogenolysis experiments were performed using a 300 ml Magne-drive autoclave (Autoclave Engineers, Inc.). The chamber was charged either inside the dry box or on the bench top using a hypodermic syringe under strong nitrogen flush. The contents were then heated and stirred under hydrogen for a predetermined period of time. After cooling to room temperature, the chamber was vented and the products were isolated inside the glove box.

Simultaneous DTA-TGA measurements were carried out on a Mettler Thermoanalyzer II. Samples were loaded in alumina or aluminum crucibles using 60 mesh alumina in the reference crucible. Heating rates between 2 and 8°/min were employed. Samples were loaded onto the thermoanalyzer under an atmosphere of argon and during the run a continuous flow of argon was maintained. Sample weight was monitored on two sensitivities (10 and 1 mg/inch) so that gross weight losses, e.g., solvent, as well as fine losses, e.g., hydrogen could be observed.

Analytical Procedures. Gas analyses were performed by hydrolyzing a measured or weighed sample inside a high vacuum line with ~ 6M hydrochloric acid and passing the evolved gases through dry ice-acetone and liquid nitrogen traps. Hydrogen was transferred to a calibrated measuring bulb with a Toepler pump. Butane was collected in a separate measured portion of the vacuum line. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as the indicator. Aluminum, when present, was masked with triethanolamine. Aluminum determinations were carried out by adding an excess of standard EDTA and then back titrating at pH 4 with standard zinc acetate in water-ethanol with dithizone as indicator. Halide determinations were performed by the Volhard titration. Alkali metals were determined by flame photometry using appropriate filters.

Materials. All solvents were distilled immediately prior to use. Tetrahydrofuran and benzene (Fisher Certified reagent grade) were distilled under nitrogen over sodium aluminum hydride and diethyl ether (Fisher reagent) over lithium aluminum hydride. Benzyl chloride (Fisher reagent grade) was distilled over P_2O_5 under reduced pressure and 2-chloropropane and 1-chloropentane (Eastman Organic Chemicals) were dried and distilled over $MgSO_4$ prior to use. Grignard grade magnesium turnings were used except in the preparation of dimethylmagnesium where triply sublimed magnesium (Dow Chemical Company) was employed. Secondary-butyllithium was obtained as a 11.9% solution in hexane from the Foote Mineral Company and stored at -20° until ready to use. Methyllithium used was a 5.0% solution in diethyl ether obtained from the Lithium Corporation of America. Lithium bromide and lithium iodide (Foote Mineral Company) were dried at

130° under vacuum for 24 hr and used without further purification. Trioctylpropyl ammonium bromide (Eastman Organic Chemicals) was dried at 55° under vacuum for 2 days and used without any subsequent purification. Ultrapure hydrogen (99.9995%) obtained from Matheson Corporation was employed in hydrogenation experiments. Dimethylmercury was obtained from Orgmet Inc., and used without further purification. Potassium hydride (as a suspension in mineral oil), lithium aluminum hydride and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Solutions of $LiAlH_4$ and $NaAlH_4$ in diethyl ether or tetrahydrofuran were prepared by making a slurry of the compounds in the respective solvents, stirring for 48 hr, and followed by centrifuging and filtration. Solutions of lithium aluminum hydride in diethyl ether were not very stable at room temperature and a progressive precipitation of small amounts of the compound was observed. All solutions were freshly analyzed immediately before use. Other materials such as active potassium hydride, disecondary-butylmagnesium, potassium di-s-butylhydridomagnesiate, trioctylpropylammonium di-s-butylhydridomagnesiate and lithium di-s-butylhydridomagnesiate were prepared according to the methods described previously.[7]

Reaction of Potassium Di-s-butylhydridomagnesiate with Lithium Bromide in Diethyl Ether. $KMgs\text{-}Bu_2H$ prepared by the reaction of potassium hydride with disecondary-butylmagnesium in benzene[7] was used for this reaction. The benzene was removed completely to give an orange-red viscous residue. This was dissolved in diethyl ether to give a clear solution and used immediately. 2.7628 g of lithium bromide (31.8 mmoles) were dissolved in 100 ml diethyl ether and added to 141.3 ml of the

KMgs-Bu_2H solution in ether (0.225 M in K^+; 31.8 mmoles) under vigorous stirring. The mixture was stirred for six hr and then filtered inside the glove box. The white precipitate was washed several times with diethyl ether, collected in a round-bottom flask and dried under vacuum at room temperature for 4 hr. The light orange filtrate on analysis gave the following ratios: Li:Mg:Bu:H = 0.56:1.00:2.0:0.50. Potassium and bromide were absent. The precipitate gave the following rations: Li:K:H:Br = 1:1.8:1:1.9.

Reaction of $LiAlH_4$ with $LiMg_2s$-Bu_4H in Diethyl Ether. 150 ml of an ether solution of $LiMg_2s$-Bu_4H (0.0576 M in Li; 8.65 mmoles) were added slowly and under stirring to lithium aluminum hydride in diethyl ether (150 ml, 0.44 M; 66 mmoles). The orange color of the mixture slowly disappeared and a white precipitate was seen to form. The stirring was continued overnight. The mixture upon filtration inside the dry box gave a white precipitate and a clear colorless filtrate. The solid was washed several times with small portions of diethyl ether and then dried under high vacuum at room temperature for 12 hr. Analysis of the solid gave the following ratios: Li:Mg:H:Bu = 1.00:2.2:4.7:0.09. Anal. - Calcd. for $LiMg_2H_5 \cdot 1(C_2H_5)_2O$:Li, 5.15; Mg, 36.10; H, 3.74; $(C_2H_5)_2O$ (by difference), 55.0. Found: Li, 4.7; Mg, 36.53; H, 3.2; $(C_2H_5)_2O$, 55.6. A very negligible quantity of magnesium was found to be present in the filtrate.

Reaction of $LiAlH_4$ with KMgs-Bu_2H in Diethyl Ether. 100 ml of a freshly prepared solution of potassium di-s-butylhydridomagnesiate (0.262 M, 26.2 mmoles) in diethyl ether were added to 32.7 ml of a lithium aluminum hydride solution in diethyl ether (0.44 M in Al, 14.4

mmoles) slowly and under stirring. An immediate yellow precipitate appeared. Another 100 ml of diethyl ether were added to the mixture and stirring was continued for 12 hr. The mixture upon filtration inside the dry box gave a yellow solid and a light orange-yellow filtrate. The solid was dried under vacuum for 12 hr. Analysis of the solid gave the following ratios: Mg:Li:K:H:Bu = 1.00:0.67:0.36:2.71:0.12. Anal. - Calcd. for $KMgH_3$ + 2 $LiMgH_3 \cdot (C_2H_5)_2O$: K, 18.7, Li, 6.64; Mg, 34.9; H, 4.34; $(C_2H_5)_2O$ (by difference), 35.43. Found: K, 18.5; Li, 6.15; Mg, 32.03; H, 3.6; $(C_2H_5)_2O$, 39.7. Analysis of the filtrate provided the balance of the reactants.

Reaction of $LiAlH_4$ with KMgs-Bu_2H in Tetrahydrofuran. 60 ml of a freshly prepared solution of KMgs-Bu_2H in tetrahydrofuran (13.3 mmoles; 0.222 M) were added to 95 ml of $LiAlH_4$ in tetrahydrofuran (0.42 M; 39.9 mmoles) slowly and with stirring. There was no immediate change. The reaction mixture was stirred overnight. An extremely small amount of cloudiness was observed. The mixture was filtered at this stage, but the amount of precipitate was almost negligible. The filtrate was concentrated by partially removing the solvent. A portion of the filtrate was refluxed for several days but no solid precipitated. To another portion, ~ 150 ml freshly distilled benzene was added and the mixture stirred. The initial orange-red color of the mixture disappeared and a white precipitate began to form. After overnight stirring, the solid was filtered, dried under vacuum for 4 hr and analyzed. The following ratios were obtained: Li:K:Al:H:Mg:Bu = 0:1.0:1.2:4.0:0.0. The filtrate analyzed for LiMgs-Bu_2H and unreacted $LiAlH_4$.

Reaction of Sodium Iodide with KMgs-Bu_2H in Tetrahydrofuran. 105 ml of a sodium iodide solution in tetrahydrofuran (0.252 M; 26.5 mmoles) were slowly added to 125 ml of a freshly prepared solution of KMgs-Bu_2H in tetrahydrofuran (25.2 mmoles in Mg). The mixture upon stirring produced a creamy yellow precipitate. The precipitation was almost instantaneous. After stirring for 4 hr the mixture was filtered and the precipitate was washed with several small portions of tetrahydrofuran. The precipitate was found to be potassium iodide upon analysis. The filtrate had a composition corresponding to NaMgs-Bu_2H.

Reaction of $NaAlH_4$ with NaMgs-Bu_2H in Tetrahydrofuran. 250 ml of a tetrahydrofuran solution of NaMgs-Bu_2H (0.0806 M in Mg, 20.14 mmoles) were added slowly to 12.4 ml (0.813 M; 10.07 mmoles) of sodium aluminum hydride in tetrahydrofuran. The mixture was kept stirred during the addition. There was no immediate change but after about 1/2 hr of stirring, a small amount of precipitate was observed. The mixture after being stirred overnight was filtered inside the dry box and the solid obtained was washed and dried for 12 hr under high vacuum. The reaction was not complete since addition of more sodium aluminum hydride to the filtrate produced a further amount of precipitate upon stirring for several hours. The solid upon analysis gave the following ratios: Na:MgH = 1.0:0.97:2.90. Anal. - Calcd. for $NaMgH_3 \cdot 0.33THF$: Na, 31.01; Mg, 32.80; H, 4.08; THF (by difference), 32.11. Found: Na, 31.55; Mg, 32.22; H, 4.02; THF, 32.21.

Reaction of $LiAlH_4$ with LiMgs-Bu_3 in Diethyl Ether. 150 ml of a benzene solution of di-secondary-butylmagnesium (0.426 M; 63.92 mmoles) were added to 53.8 ml of a hexane solution of s-butyllithium (1.189 M;

63.92 mmoles). After stirring the mixture for 2 hr at 25°, the solvents were removed under vacuum. 200 ml diethyl ether was added to the yellow orange oily residue. A yellow precipitate resulted immediately. To the stirred suspension, 75 ml of $LiAlH_4$ in diethyl ether (1.28 M; 96 mmoles) were added slowly under stirring. A white precipitate resulted immediately upon the addition. After 2 hr of stirring, the solid was filtered and washed with diethyl ether. Analysis gave the following ratios in the solid: Li:Mg:H = 1.17:1.00:2.92 (after subtracting for some $LiAlH_4$ carried over in the precipitate). Anal. - Calcd. for $4\ LiMgH_3 \cdot LiAlH_4 \cdot 1.55(C_2H_5)_2O$: Li, 12.0; Mg, 33.54; Al, 9.31; H, 5.56; $(C_2H_5)_2O$. Found: Li, 13.44; Mg, 32.82; Al, 9.40; H, 5.60; $(C_2H_5)_2O$, 38.75.

Preparation of Dimethylmagnesium in Diethyl Ether. Dimethylmercury (26.31 ml; 350 mmoles) was added to triply sublimed magnesium (17.02 g; 700 mmoles) in a 500 ml three-necked round bottom flask equipped with a dry ice-acetone condenser. The reaction was almost spontaneous and the initial heat release ended after one hour. The flask was allowed to sit for 12 hr and then placed under vacuum for 4 hr at 55° to remove any unreacted dimethylmercury. The resulting fluffy white dimethylmagnesium was extracted with diethyl ether and separated from the residual magnesium amalgam by filtration. Analysis of the filtrate indicated the solution to be 0.634 M in magnesium. The test for mercury was negative.

Reaction of $LiAlH_4$ with $Li_2Mg(CH_3)_4$ in Diethyl Ether. 25 mmoles of dimethylmagnesium (39.4 ml; 0.634 M) were diluted with 100 ml diethyl ether and added to 49.6 ml methyllithium in diethyl ether (1.01 M; 50 mmoles). The mixture was stirred at -78° (dry ice-acetone) for 2 hr and then added

to 39.2 ml $LiAlH_4$ (1,275 M; 50 mmoles) in diethyl ether at -78°. An immediate white precipitate resulted. After stirring the mixture for 4 hr at low temperature, filtration was carried out to separate the solid. About 250 ml of diethyl ether were used for washing the solid. The solid was dried for 5 hr under vacuum. Analysis gave the following ratios (after deducting the $LiAlH_4$ carried over in the solid): Li:Mg:H = 1.96:1.00:3.97. Anal. - Calcd. for 7 $Li_2MgH_4 \cdot LiAlH_4 \cdot 2.6(C_2H_5)_2O$: Li, 19.78; Mg, 32,34; Al, 5.13; H, 6.13; $(C_2H_5)_2O$, 36.62. Found: Li, 19.45; Mg, 32.37; Al, 5.23; H, 6.11; $(C_2H_5)_2O$, 36.84. There was no magnesium in the filtrate.

Reaction of $LiAlH_4$ with $Li_3Mg(CH_3)_5$ in Diethyl Ether. 75 mmoles of methyllithium in diethyl ether were added to 25 mmoles (39.4 ml; 0.634 M) dimethylmagnesium in diethyl ether. The mixture was diluted with 135 ml diethyl ether and stirred at -78° for one hour. The resulting clear solution was added to 49.0 ml (62.4 mmoles; 1.275 M) of $LiAlH_4$ in diethyl ether at -78° under stirring. A white precipitate formed immediately upon the addition. Stirring was continued for 2 1/2 hr at -78°. The solid was filtered, washed with ~ 250 ml diethyl ether and dried under vacuum for 12 hr. Elemental analysis indicated the following ratios (after subtracting the $LiAlH_4$ carried over with the precipitate): Li:Mg:H = 2.91:1.00:4.90. Anal. - Calcd. for 2.4 $Li_3MgH_5 \cdot 1\ LiAlH_4 \cdot 0.41\ (C_2H_5)_2O$: Li, 30.15, Mg, 30.91; Al, 14.29; H, 8.54; $(C_2H_5)_2O$, 16.10. Found: Li, 29.63; Mg, 31.15; Al, 14.46; H, 8.49; $(C_2H_5)_2O$, 16.27. No magnesium was detected in the filtrate.

Results and Discussion

The preparation of several new complex metal hydrides of magnesium has been possible by first reacting potassium hydride with di-s-butylmagnesium in benzene to give $KMg(s\text{-}Bu)_2H$ and then making the lithium, sodium and tetralkylammonium derivatives by metathetical exchange reactions.

$$KH + (s\text{-}Bu)_2Mg \xrightarrow[R.T.]{\emptyset H} KMg(s\text{-}Bu)_2H \xrightarrow[\text{or THF}]{NR_4Br,\ \emptyset H} NR_4MgR_2H + KBr\downarrow \quad (R = C_8H_{17}C_3H_7) \qquad (1)$$

$$KMg(s\text{-}Bu)_2H + LiBr \xrightarrow[R.T.]{THF} LiMg(s\text{-}Bu)_2H + KBr\downarrow \qquad (2)$$

$$2\ KMg(s\text{-}Bu)_2H + 2\ LiBr \xrightarrow[R.T.]{(C_2H_5)_2O} LiMg_2(s\text{-}Bu)_4H + 2\ KBr\downarrow + LiH\downarrow \qquad (3)$$

$$KMg(s\text{-}Bu)_2H + NaI \xrightarrow[R.T.]{THF} NaMg(s\text{-}Bu)_2H + KI\downarrow \qquad (4)$$

This procedure is extremely useful since, in contrast to KH, LiH does not react directly with alkylmagnesium compounds. Also, this is the only possible route for making a 1:1 complex of NaH with R_2Mg since sodium hydride reacts directly with R_2Mg in benzene to give only the 1:2 adduct:

$$NaH + 2(s\text{-}Bu)_2Mg \xrightarrow{\emptyset H} NaMg_2(s\text{-}Bu)_4H \qquad (5)$$

The reduction of $MMgR_2H$ type compounds with a suitable alkali metal aluminum hydride allows for a more convenient method of conversion of M-R to M-H compounds without having to resort to high pressure hydrogenation. Since the preparation of $LiMg(s\text{-}Bu)_2H$, $NaMg(s\text{-}Bu)_2H$ and $LiMg_2(s\text{-}Bu)_4H$ can only be carried out in ether solvents and since complete solvent removal still leaves traces of ether in the compound, partial or

complete cleavage of the reaction products is produced on high pressure hydrogenation.[7] A solution to this problem lies in the fact that reduction of $MMgR_2H$ compounds can be carried out with alkali metal aluminum hydrides at low temperature. Since the reaction is extremely fast, even at low temperature, no cleavage products result. The advantages of such chemical reductions are indeed very great.

When $KMg(s\text{-}Bu)_2H$ is made by reacting KH with $s\text{-}Bu_2Mg$ in benzene, and the solvent removed, the oily product obtained dissolves readily in tetrahydrofuran or diethyl ether. The stability of the compound is not very great in ether solution at room temperature; however, solutions can be stored and used at low temperature after several days without any apparent cleavage or decomposition. There is an interesting basic difference between the reactions of $KMg(s\text{-}Bu)_2H$ with lithium bromide in THF and diethyl ether. In the case of tetrahydrofuran, $LiMg(s\text{-}Bu)_2H$ results (eq. 2) but when diethyl ether is used, $LiMg_2(s\text{-}Bu)_4H$ is the product (eq. 3). The solid obtained from reaction in eq. 3 was analyzed and found to be a mixture of 2 KBr and 1 LiH. It seems that $LiMg(s\text{-}Bu)_2H$ is perhaps formed in this reaction, but that it slowly disproportionates into $LiMg_2(s\text{-}Bu)_4H$ + LiH during the course of the reaction.

When lithium aluminum hydride was added to the $LiMg_2(s\text{-}C_4H_9)_4H$ in diethyl ether, a white precipitate formed spontaneously. Analysis of the solid revealed the composition to be $LiMg_2H_5 \cdot (C_2H_5)_2O$. No aluminum was detected in the solid.

$$LiMg_2(s\text{-}C_4H_9)_4H + 3\ LiAlH_4 \longrightarrow LiMg_2H_5 + 3\ LiAl(C_4H_9)_2H_2 \qquad (6)$$

The X-ray powder diffraction of the solid (Table II) showed only five lines which were broad and diffused indicating the amorphous nature of the compound. However, these lines were centered at unique positions and lines due to LiH and MgH_2 were absent. Thus, the compound is not a physical mixture of LiH and MgH_2 (Table I) but a definite complex.

The reaction of lithium aluminum hydride with $KMg(s\text{-}Bu)_2H$ in diethyl ether does not proceed as would be expected:

$$KMg(s\text{-}Bu)_2H + LiAlH_4 \xrightarrow{(C_2H_5)_2O} KMgH_3\downarrow + LiAl(s\text{-}Bu)_2H_2 \qquad (7)$$

Instead, a solid is obtained with a composition $2\ LiMgH_3 \cdot KMgH_3 \cdot 1(C_2H_5)_2O$. It seems that the reaction, in reality, proceeds as follows:

$$3\ KMg(s\text{-}Bu)_2H + 3\ LiAlH_4 \xrightarrow{(C_2H_5)_2O} KMgH_3 + 2\ LiMgH_3 + LiAlR_2H_2 + KAlR_2H_2 \qquad (8)$$

Cation exchange apparently occurs in this reaction. X-ray powder pattern of the solid (Table II) showed few lines, due to the lack of crystallinity. However, half of the lines observed could be attributed to $KMgH_3$ based on the X-ray pattern of an authentic sample of $KMgH_3$ (Table I). Two lines were new and could be attributed to $LiMgH_3$. Characterization of this mixture is being carried out by simultaneous DTA-TGA analysis.

When lithium aluminum hydride was allowed to react with $KMg(s\text{-}Bu)_2H$ in tetrahydrofuran the cation exchange again takes place but no product precipitate. The reaction can be described by the following equation:

$$KMg(s\text{-}Bu)_2H + LiAlH_4 \longrightarrow KAlH_4 + LiMg(s\text{-}Bu)_2H \qquad (9)$$

When benzene is added to the clear solution, $KAlH_4$ precipitates. The precipitate was analyzed and showed a ratio K:Al:H = 1:1.2:4.0. No magnesium,

butane or lithium was present in the solid.

Upon the addition of sodium iodide to $KMg(s\text{-}Bu)_2H$ in tetrahydrofuran, a quantitative precipitate of KI is obtained (eq. 4). Addition of sodium aluminum hydride to the filtrate ($NaMgs\text{-}Bu_2H$), resulted in the slow precipitation of a white solid. Analysis indicated the solid to be $NaMgH_3 \cdot 0.33THF$.

$$2\ NaMg(s\text{-}Bu)_2H + NaAlH_4 \longrightarrow 2\ NaMgH_3\downarrow + NaAl(s\text{-}Bu)_4 \qquad (10)$$

The X-ray powder data for this compound are described in Table II. There were no lines due to NaH or MgH_2 (Table I) indicating that the compound is indeed $NaMgH_3$ and not a physical mixture of NaH and MgH_2. The infrared spectrum of the solid in nujol showed the characteristic broad absorption bands in the Mg-H stretching and deformation regions.

When s-butyllithium was added to di-s-butylmagnesium in hydrocarbon media, an authentic 1:1 complex $LiMg(s\text{-}C_4H_9)_3$ was formed. This complex was prepared by stirring s-BuLi in hexane with a stoichiometric amount of di-s-butylmagnesium in benzene. Upon removal of the solvent under reduced pressure, a light yellow oily residue was obtained. Diethyl ether was added to this oily product, whereupon a yellow solid precipitated. When $LiAlH_4$ in diethyl ether was added to this suspension, a white solid was produced which upon analysis gave the composition as $4\ LiMgH_3 \cdot 1\ LiAlH_4 \cdot 1.55(C_2H_5)_2O$.

$$4\ LiMg(s\text{-}C_4H_9)_3 + 4\ LiAlH_4 \longrightarrow 4\ LiMgH_3 \cdot LiAlH_4 + 3\ LiAl(s\text{-}C_4H_9)_4 \qquad (11)$$

An X-ray Powder diffraction pattern of the solid (Table III) showed few lines, and many of these corresponded with LiH except one line which was new. Thus,

it appears that the compound is a mixture of LiH and MgH_2 and perhaps there is some $LiMgH_3$ present. It is not definite whether $LiMgH_3$ can be prepared through such a reaction. DTA-TGA studies of this compound are in progress.

When methyllithium is added to dimethylmagnesium in diethyl ether, a series of complexes of the type $Li_xMg_y(CH_3)_{x+2y}$ is formed depending upon the stoichiometry of the reactants. At low temperatures the complexes are essentially undissociated. However, there is no evidence for the formation of a 1:1 complex, i.e., $LiMg(CH_3)_3$.[9]

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(9) L. M. Seitz and T. L. Brown, J. Amer. Chem. Soc., 88, 4140 (1966).

$$2\ CH_3Li + (CH_3)_2Mg \longrightarrow Li_2Mg(CH_3)_4 \qquad (12)$$

$$3\ CH_3Li + (CH_3)_2Mg \longrightarrow Li_3Mg(CH_3)_5 \qquad (13)$$

It was thought of interest to attempt the reduction of these complexes with lithium aluminum hydride to form the complex magnesium hydrides.

When $LiAlH_4$ was added to a mixture of 2:1 methyllithium:dimethylmagnesium at -78° (dry ice-acetone), a white precipitate formed spontaneously.

$$Li_2Mg(CH_3)_4 + 2\ LiAlH_4 \longrightarrow Li_2MgH_4 + 2\ LiAl(CH_3)_2H_2 \qquad (14)$$

The solid upon analysis gave the following composition: $7\ Li_2MgH_4 \cdot 1\ LiAlH_4 \cdot 2.6(C_2H_5)_2O$. The X-ray powder diffraction pattern showed very well defined lines as outlined in Table III. The strongest lines due to LiH and MgH_2 (Table I) were clearly absent indicating that the solid was not a physical mixture of LiH and MgH_2, and was indeed Li_2MgH_4.

When lithium aluminum hydride was added to a 3:1 mixture of methyllithium and dimethylmagnesium at -78°, an immediate white precipitate resulted.

$$2\ Li_3Mg(CH_3)_5 + 5\ LiAlH_4 \longrightarrow 2\ Li_3MgH_5 + 5\ LiAl(CH_3)_2H_2 \qquad (15)$$

The white solid obtained upon filtration analyzed for $2.4\ Li_3MgH_5 \cdot 1\ LiAlH_4 \cdot 0.4(C_2H_5)_2O$. X-ray powder diffraction showed unique lines (Table III) and none due to either LiH or MgH_2 were present. Thus, the compound is in fact Li_3MgH_5 and not a physical mixture of LiH and MgH_2.

It has been observed that lithium aluminum hydride reductions of the Li-Mg-R compounds in diethyl ether produce Li-Mg hydrides which have varying degrees of solid $LiAlH_4$ present in them, depending upon the reaction conditions, washing of the precipitate, etc. An effort to separate this lithium aluminum hydride from the Li-Mg hydrides is being carried out.

Thermal decomposition studies on the compounds described in this paper are presently in progress.

Table I. X-Ray Powder Diffraction Data (Reference Compounds)

LiH	KH	NaH	MgH_2	$KMgH_3$	$KMgF_3$
4.36 vvw	3.30 vs	5.72 vvw	3.19 vs	4.003 vw	
2.76 vvw	2.86 s	3.13 w	2.76 vw	3.137 vvw	
2.66 vvw	2.02 s	3.03 vw	2.495 vs	2.835 vs	2.80 m
2.50 vvw	1.72 s	2.82 vs	2.29 m	2.311 m	2.29 m
2.36 s	1.43 m	2.72 vw	1.59 s	2.007 s	1.99 vs
2.25 vvw	1.65 m	2.44 s	1.67 s	1.794 vw	
2.04 s	1.31 m	2.37 w	1.50 m	1.639 s	1.625 m
1.63 vvw	1.28 m	1.73 m	1.42 w	1.420 m	1.408 m
1.44 ms	1.17 m	1.63 vw	1.36 w	1.268 m	1.259 w
1.23 m	1.10 m	1.47 m	1.335 w	1.184 m	1.201 s
1.18 mw	1.01 w	1.41 w	1.246 w	1.158 w	1.150 w
1.02 w		1.22 w	1.150 w	1.122 vw	
0.94 w		1.12 w	1.125 w		
0.91 w		1.09 w			
0.834 w					
0.832 vw					
0.786 vw					
0.784 vw					

w. weak; m, medium; s, strong; v, very

Table II. X-Ray Powder Diffraction Data

$KMgH_3$ + 2 $LiMgH_3 \cdot (C_2H_5)_2O$		$LiMg_2H_5 \cdot (C_2H_5)_2O$		$NaMgH_3 \cdot 0.33THF$	
4.85 - 4.90	m	4.70	m,d	3.80	vw
3.13	m	2.30	m,d	3.00	vw
2.83	w	1.53	m,d	2.73	vs
2.22	vw	0.868	m,d	1.92	m
		0.834	m,d	1.72	vvw
				1.56	s
				1.355	w
				1.212	w
				1.025	w
				0.903	vw
				0.857	vw
				0.836	vvw

w, weak; m, medium; s, strong; v, very; d, diffused

Table III. X-Ray Powder Diffraction Data

" "$LiMgH_3$"		Li_2MgH_4		Li_3MgH_5	
4.85 - 4.90	ms	4.32	m	4 - 5	vw,d
2.33	m	4.20	m	2.95	mw
2.47	vw	4.05	ms	2.55	mw
2.03	ms	3.72	w	2.35	mw,d
1.44	vw	3.65	w	2.05	mw,d
		2.73	vs	1.82	vw
		2.49	ms	1.45	vw,d
		1.76	m	0.865	vw,d
		1.638	w	0.840	vw,d
		1.48	w		
		1.26	vw		
		0.862	vvw,d		
		0.838	vvw,d		

w, weak; m, medium; s, strong; v, very; d, diffused

Synthesis of Complex Metal Hydrides of Zinc

E. C. Ashby and John J. Watkins

Abstract

A series of complex metal hydrides of zinc with composition $M_nZn_mH_{2m+n}$, where M = Li, Na, or K, have been synthesized by reacting an appropriate "ate" complex of zinc with either $LiAlH_4$, $NaAlH_4$, or AlH_3. The 1:1, 2:1, and 3:1 complexes of methyllithium with dimethylzinc yielded $LiZnH_3$, Li_2ZnH_4, and Li_3ZnH_5 when reacted with lithium aluminum hydride in diethyl ether. The reaction of potassium hydride with dimethylzinc in 1:1 and 1:2 ratios in tetrahydrofuran yielded potassium dimethylhydridozincate [$KZn(CH_3)_2H$] and potassium tetramethylhydridodizincate [$KZn_2(CH_3)_4H$]. KZn_2H_5 resulted when either $KZn(CH_3)_2H$ or $KZn_2(CH_3)_4H$ were allowed to react with alane in tetrahydrofuran; whereas, $KZnH_3$ was obtained from the reaction of $KZn(CH_3)_2H$ with lithium aluminum hydride in tetrahydrofuran. Both the 1:1 and 1:2 complexes of sodium hydride with dimethylzinc gave sodium trihydridozincate when allowed to react with sodium aluminum hydride in tetrahydrofuran. All these reactions are presented as examples of a new and general route for the preparation of complex metal hydrides by the reaction of a properly selected "ate" complex of a particular metal with complex metal hydrides of aluminum.

Introduction

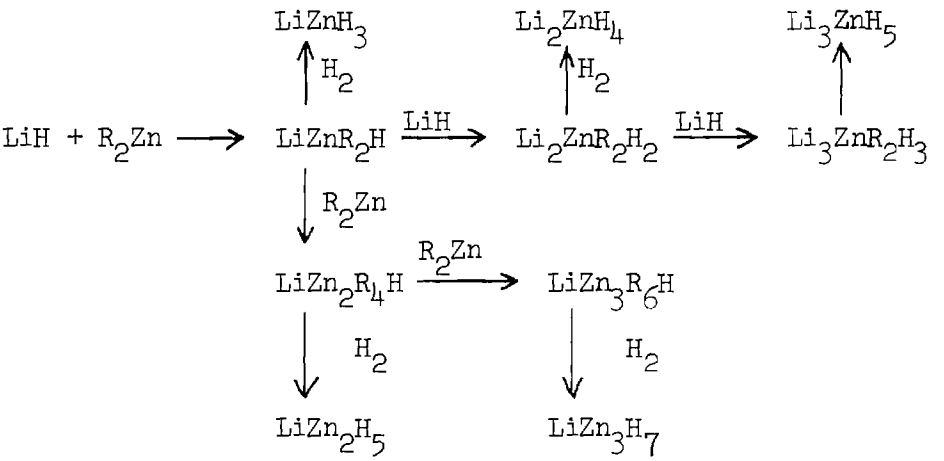
In view of our recent reports of the synthesis of $KMg(s\text{-}C_4H_9)_2H$, $KMgH_3$,[1,2] K_2ZnH_4, and Na_2ZnH_4,[3] we wished to expand our synthetic studies

(1) E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 21, 29 (1970).

(2) E. C. Ashby, R. Kovar and R. C. Arnott, J. Amer. Chem. Soc., 92, 2182 (1970).

(3) E. C. Ashby and R. G. Beach, Inorg. Chem., 10, 2486 (1971).

to include other complex metal hydrides of zinc. Our initial plan was to investigate the reaction of LiH with di-s-butylzinc in both hydrocarbon and ether solvents in an attempt to prepare a spectrum of lithium dialkylzinc hydrides ranging from $Li_2ZnR_2H_3$ to $LiZn_3R_6H$, where R = s-butyl. The lithium dialkylzinc hydrides were to be converted to the corresponding complex metal hydrides by high pressure hydrogenation, since the carbon-zinc bond of the s-butyl-zinc group should be easily converted to a H-Zn bond by hydrogenation. The series of reactions below outline the proposed synthetic scheme for the preparation of a series of lithium zinc hydrides. The logical extension of this synthetic scheme would then be to prepare



some of the corresponding sodium and potassium zinc hydrides by a similar series of reactions.

Our initial plan became unfeasible very quickly and had to be

modified, since the intermediate lithium s-butylzinc hydrides were found to cleave ether solvents too rapidly for hydrogenation to be an effective tool for R-Zn to H-Zn conversion. The plan was modified in two ways. First, lithium aluminum hydride was used as the reducing agent, since alkyl exchange from zinc to aluminum and hydrogen exchange from aluminum to zinc might be expected at temperatures lower than 0°C. At these temperatures the starting lithium alkylzinc hydrides should not be cleaving ether solvents. Second, dimethylzinc could be used as a starting material rather than di-s-butylzinc since methyl group exchange should be easier compared to s-butyl group exchange. In addition, Shriver and coworkers,[4] in their report on the preparation and properties

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(4) G. J. Kubas and D. F. Shriver, J. Amer. Chem. Soc., 92, 1949 (1970).

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of $MZnR_2H$ compounds, showed that $LiZn(CH_3)_2H$ and $NaZn(CH_3)_2H$ are better defined species in solution than the higher alkyl analogues.

The complex metal hydrides of zinc described in this report should be of considerable interest as new compositions involving complex metal hydrides of Group II B elements. In addition, these compounds are of interest from a structural view point, as selective reducing agents in organic chemistry and as polymerization catalysts.

Experimental

Apparatus - Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a circulating system using manganese oxide columns to remove oxygen

and dry ice-acetone to remove solvent vapors.[5]

(5) D. F. Shriver, "The Manipulations of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

Infrared spectra were obtained using a Perkin Elmer 621 Spectrophotometer as Nujol mulls between CsI plates. X-ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered CuK_{α} radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hrs. D-spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300 ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high pressure hydrogenation.

Analytical - Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was carried out by masking the aluminum with triethanolamine and titrating the zinc with EDTA.

Materials - Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of t-butyllithium at 4000 psig for 24 hours. Solutions of lithium and sodium aluminum hydride (Ventron, Metal Hydride Division) were prepared in both diethyl ether and tetrahydrofuran in the usual manner. Dimethyl- and di-s-butylzinc were prepared by the Noller procedure.[6] Methyl and s-butyl iodides were obtained from Fisher Scientific.

(6) C. R. Noller, Org. Syn., 12, 86 (1932).

The iodides were dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc-copper couple was obtained from Alfa Inorganics and the reactions with methyl iodide were allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture at atmospheric pressure under nitrogen while di-s-butylzinc was distilled at reduced pressure. Methyl lithium (made from CH_3Cl) was obtained as a 5% solution in ether from Matheson, Coleman, and Bell and stored at -20° until ready to use. Tetrahydrofuran and benzene (Fisher Certified Reagent Grade) were distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher Reagent) over lithium aluminum hydride. Ultra-pure hydrogen (99.9995%) obtained from the Matheson Corporation was used for hydrogenation experiments.

Reaction of LiH and $(s\text{-}C_4H_9)_2Zn$ in Benzene. Di-s-butylzinc (66 mmoles) in benzene was added to a slurry of LiH (66 mmoles) in benzene. After stirring for one week, the mixture was filtered. The filtrate showed a Zn:s-butyl ratio of 1:1.98, but no lithium or hydridic hydrogen was found. The solid analyzed for Li:Zn:H ratios of 10:1:7.

Reaction of LiH and $(s\text{-}C_4H_9)_2Zn$ in Tetrahydrofuran. 27.9 mmoles of di-s-butylzinc in tetrahydrofuran was added to 27.9 mmoles of a LiH slurry in tetrahydrofuran. The mixture was stirred at room temperature overnight. A clear solution resulted which exhibited a Li:Zn:s-C_4H_9:H ratio of 1.00:0.96:1.88:0.32. A gas chromatograph of a hydrolyzed portion showed a large butanol peak due to extensive ether cleavage. A similar reaction was run where all the tetrahydrofuran was stripped off as soon as the lithium hydride dissolved. But the lithium di-s-butylhydridozincate complex decomposed to lithium hydride and di-s-butylzinc under vacuum. Thus, it was not possible to remove all the tetra-

hydrofuran and dissolve the residue in a non-cleaving solvent, such as benzene.

Reaction of LiH and $(s\text{-}C_4H_9)_2Zn$ in Diethyl Ether. 28 mmoles of di-s-butylzinc in diethyl ether was added to a slurry of 28 mmoles of LiH in diethyl ether. The mixture was stirred for one week and filtered. The filtrate showed a Li:Zn ratio of 0.20:1.00. The solid exhibited a Li:Zn:H ratio of 1.00:0.06:0.97. The reaction was repeated under reflux conditions for two weeks. Still no reaction occurred.

Preparation of Li_2ZnH_4 by $LiAlH_4$ Reduction of $LiZn(s\text{-}C_4H_9)_2H$ in Tetrahydrofuran. 5.49 mmoles of LiH slurry in tetrahydrofuran were added to 5.49 mmoles of di-s-butylzinc in tetrahydrofuran. This mixture was stirred until all the lithium hydride went into solution (about 21 hours), then 8.11 mmoles of $LiAlH_4$ in tetrahydrofuran was added immediately. After five minutes a white solid began to appear; and after 30 minutes the mixture had a slightly gray, thick, milky appearance. The mixture was stirred overnight at room temperature. The solid, now having a gray appearance, was separated by filtration and dried at room temperature in vacuo. Anal. Calcd. for Li_2ZnH_4: Li, 16.7; Zn, 78.5; H, 4.85. Found: Li, 16.3; Zn, 79.5; H, 4.11. The molar ratio of Li:Zn:H is 1.93:1.00:3.36. The filtrate contained 8.50 mmoles of aluminum, 3.40 mmoles of zinc, and 10.31 mmoles of lithium. The amount of Li_2ZnH_4 recovered was 2.09 mmoles of a theoretical 2.75 mmoles. The X-ray powder diffraction data is given in Table 1. Infrared spectrum (Nujol mull) showed two strong broad bands at 400-1000 cm^{-1} centered at 650 cm^{-1} and 1200-1650 cm^{-1} centered at 1450 cm^{-1}. This spectrum was very similar to that found for K_2ZnH_4.[3]

Attempted Preparation of $LiZnH_3$ by Reaction of $LiZn(CH_3)_2H$ with $LiAlH_4$ in Tetrahydrofuran. 10 mmoles of dimethylzinc in tetrahydrofuran was added to 10 mmoles of a LiH slurry in tetrahydrofuran. After five hours stirring the solution was clear. 10 mmoles of $LiAlH_4$ in tetrahydrofuran was added quickly. After one minute the solution became faintly cloudy; and after 30 minutes a thick white mixture was present. The mixture was stirred overnight at room temperature and filtered the next day. The precipitate, which had now become very gray due to decomposition to zinc metal, was dried at room temperature in vacuo. Anal. Calcd. for $LiZnH_3$: Li, 9.2; Zn, 86.8; H, 4.0. Found: Li, 9.4; Zn, 87.2; H, 3.35. The molar ratio of Li:Zn:H was 1.00:1.00:2.51. The filtrate contained 10.78 mmoles of aluminum, 1.41 mmoles of zinc, and 11.20 mmoles of lithium. The amount of solid recovered was 8.59 mmoles of a theoretical 10 mmoles. The X-ray powder diffraction data which is given in Table 1 showed lines for Li_2ZnH_4 and zinc metal only.

Attempted Preparation of $Li_2Zn(CH_3)_2H_2$ in Tetrahydrofuran. 20 mmoles of lithium hydride slurry in THF was added to 10 mmoles of dimethylzinc in tetrahydrofuran. The resulting mixture was stirred for two weeks at room temperature. A solid was always present. The solid was separated by filtration and dried at room temperature in vacuo. The solid had a molar ratio of Li:Zn of 15.22:1.00. The X-ray powder diffraction pattern contained lines due to lithium hydride and zinc metal only. The Li:Zn ratio of the filtrate was 1.28:1.00.

Attempted Preparation of $LiZn_2H_5$ by Reaction of $LiZn_2(CH_3)_4H$ with $LiAlH_4$ in Tetrahydrofuran. 5 mmoles of a lithium hydride slurry in tetrahydrofuran was added to 10 mmoles of dimethylzinc in tetrahydrofuran.

Five minutes later a clear solution was present. 9.57 mmoles of $LiAlH_4$ was added quickly. No immediate reaction was observable, but after 30 minutes some gray solids began to appear. The mixture was stirred overnight at room temperature. The next day, very gray almost black solids were present. The precipitate was separated by filtration and dried at room temperature in vacuo. The molar ratio of Li:Zn:H in the solid was 1.00:3.89:4.99. The filtrate contained 10.20 mmoles of aluminum, 5.49 mmoles of zinc, and 13.81 moles of lithium. X-ray powder diffraction data for the solid which is given in Table 1 showed lines for Li_2ZnH_4 and zinc metal only. Infrared analysis (Nujol mull) of the solid showed three broad bands (400-700 cm^{-1}, 950-1150 cm^{-1}, and 1350-2000 cm^{-1}).

Preparation of Li_2ZnH_4 by Reaction of $LiAlH_4$ with $Li_2Zn(CH_3)_4$ in Diethyl Ether. 10 mmoles of dimethylzinc in diethyl ether was added to 20 mmoles of methyllithium in diethyl ether. The resulting solution was stirred for one hour at room temperature followed by addition of 20 mmoles of $LiAlH_4$ in diethyl ether. White solids appeared immediately, indicating that the exchange of methyl- for hydrido-groups between zinc and aluminum was very rapid. This mixture was stirred for one hour at room temperature and then filtered. The resulting white solid was dried at room temperature in vacuo. Anal. Calcd. for Li_2ZnH_4: Li, 16.7; Zn, 78.5; H, 4.85. Found: Li, 14.8, Zn, 80.4; H, 4.85. The molar ratio of Li:Zn:H was 1.73:1.00:3.94. The filtrate contained 19.30 mmoles of aluminum, no zinc, and 20.01 mmoles of lithium. The amount of Li_2ZnH_4 recovered was 10 mmoles of a theoretical 10 mmoles. The X-ray powder diffraction data is given in Table 1. Infrared analysis (Nujol mull) showed three broad bands (400-900 cm^{-1}, 1200-1400 cm^{-1} centered at

1290 cm^{-1}, and 1400-1900 cm^{-1} centered at 1580 cm^{-1}). Infrared analysis of the filtrate (KBr cell 0.10 mm path-length) showed a strong peak in the Al-H stretching region centered at 1700 cm^{-1} and a moderate peak in the Al-H deformation region centered at 760 cm^{-1}. This spectrum is characteristic of the species $LiAl(CH_3)_2H_2$.

Preparation of Li_3ZnH_5 by Reaction of $LiAlH_4$ with $Li_3Zn(CH_3)_5$ in Diethyl Ether. 15 mmoles of methyllithium in diethyl ether was added to 5 mmoles of dimethylzinc in diethyl ether. The resulting solution was stirred for one hour at room temperature followed by addition of 12.5 mmoles of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. The mixture was stirred for one hour more at room temperature and then filtered. The resulting white solid was dried at room temperature in vacuo and analyzed. Anal. Calcd. for Li_3ZnH_4: Li, 22.9; Zn, 71.6; H, 5.53. Found: Li, 20.8; Zn, 71.5; H, 5.47; Al, 2.01. The molar ratio of $Li:Zn:H:LiAlH_4$ was 2.67:1.00:4.88:0.068. The filtrate contained 11.92 mmoles of aluminum, no zinc, and 13.42 mmoles of lithium. The molar ratio of Li:Al:Zn in the filtrate was 1.12:1.00:0.00. The amount of Li_3ZnH_5 recovered was 5 mmoles of a theoretical 5 mmoles. The X-ray powder diffraction data is given in Table 1. Infrared analysis of the solid (Nujol mull) showed two strong bands at 400-950 cm^{-1} centered at 680 cm^{-1} and 1400-1900 cm^{-1} centered at 1550 cm^{-1} and two moderate bands at 950-1100 cm^{-1} centered at 990 cm^{-1} and 1150-1450 cm^{-1} centered at 1280 cm^{-1}.

Preparation of $LiZnH_3$ by Reaction of $LiAlH_4$ with $LiZn(CH_3)_3$ in Diethyl Ether. 5 mmoles of methyllithium in diethyl ether were added to 5 mmoles of dimethylzinc in diethyl ether. The resulting solution was

stirred at room temperature for one hour, then 7.5 mmoles of $LiAlH_4$ in diethyl ether was added. A white precipitate appeared immediately. This mixture was stirred at room temperature for another hour and filtered. The white solid was dried at room temperature in vacuo and analyzed. Anal. Calcd. for $LiZnH_3$: Li, 9.2; Zn, 86.8; H, 4.0. Found: Li, 9.2; Zn, 86.5; H, 4.30. The molar ratio of Li:Zn:H was 1.00:1.00:3.21. The filtrate contained 7.53 mmoles of aluminum, no zinc, and 7.34 mmoles of lithium. The amount of $LiZnH_3$ recovered was 5 mmoles of a theoretical 5 mmoles. The X-ray powder diffraction data is given in Table 1.

Attempted Preparation of $LiZn_2H_5$ by Reaction of $LiAlH_4$ with $LiZn_2(CH_3)_5$ in Diethyl Ether. 5 mmoles of methyllithium in diethyl ether was added to 10 mmoles of dimethylzinc in diethyl ether. The resulting solution was stirred for one hour at room temperature, then 12.5 mmoles of $LiAlH_4$ in diethyl ether were added. A white precipitate appeared immediately. This mixture was then stirred for an additional hour and filtered. The solid which was a little gray at this point was dried under vacuum at room temperature. Anal. Calcd. for $LiZn_2H_5$: Li, 4.86; Zn, 91.6; H, 3.54. Found: Li, 5.08; Zn, 91.6; H, 3.45. The molar ratio of Li:Zn:H was 1.00:1.92:4.66. The filtrate contained 12.55 mmoles of aluminum, 0.04 mmoles of zinc, and 12.59 mmoles of lithium. The amount of solid recovered was 5 mmoles of a theoretical 5 mmoles. The X-ray powder diffraction data is given in Table 1.

Attempted Preparation of $LiZn_3H_7$ by Reaction of $LiAlH_4$ with $LiZn_3(CH_3)_7$ in Diethyl Ether. 15 mmoles of dimethylzinc in diethyl ether was added to 5 mmoles of methyllithium in diethyl ether. The resulting solution was stirred for one hour at room temperature followed by addition

of 17.5 mmoles of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. This mixture was stirred for an hour and filtered. The solid, which had turned slightly gray, was dried under vacuum at room temperature. Anal. Calcd. for $LiZn_3H_7$: Li, 3.30; Zn, 93.4; H, 3.36. Found: Li, 3.11; Zn, 93.6; H, 3.34. The molar ratio of Li:Zn:H was 1.00:3.20:7.37. The filtrate contained 18.02 mmoles of aluminum, no zinc, and 18.20 mmoles of lithium. The yield of solid was 100%. The X-ray powder diffraction data is given in Table 1.

Reaction of KH and $(CH_3)_2Zn$ in Diethyl Ether. 26.73 mmoles of dimethylzinc in diethyl ether were added to a slurry of 60.4 mmoles of potassium hydride in diethyl ether. The slurry became hot immediately and solvent came to reflux. A solid was always present during the reaction. The mixture was stirred overnight at room temperature and filtered the next day. The resulting white solid was dried under vacuum at room temperature. The X-ray powder diffraction data is given in Table 2. The filtrate showed a molar ratio of K:Zn of 0.92:1.00, but it contained only 0.59 mmoles of zinc, i.e., only 2.22% of the starting zinc was found in the filtrate. The solid was slurried for three hours in tetrahydrofuran, then filtered. The residual solid was shown to be KH by X-ray powder diffraction and the filtrate had a molar ratio of $K:Zn:CH_3:H$ of 0.98:1.00:2.14:0.39. The $KZn(CH_3)_2H$ formed was insoluble in diethyl ether but soluble in tetrahydrofuran at room temperature.

Attempted Preparation of $K_2Zn(CH_3)_2H_2$ in Tetrahydrofuran. 19.67 mmoles of dimethylzinc in tetrahydrofuran were added to 39.35 mmoles of a potassium hydride slurry in tetrahydrofuran. The mixture was stirred for two hours at room temperature and the next two hours at

-80°. (This should have been enough time for reaction to take place, since the 1:1 complex forms within one minute at room temperature.) A sample of the supernatant had a molar ratio of K:Zn of 0.949:1.00.

Preparation of KZn_2H_5 by Reaction of AlH_3 with $KZn(CH_3)_2H$ in Tetrahydrofuran. 10 mmoles of dimethylzinc in tetrahydrofuran were was added to 10 mmoles of a slurry of KH in tetrahydrofuran at room temperature. The mixture was clear within one minute. The mixture was quickly cooled to -80° to prevent ether cleavage, and stirred for two additional hours. Next, 10 mmoles of AlH_3 in tetrahydrofuran was added to the solution which was still at -80°. The bath was removed and the reaction allowed to warm to room temperature. After fifteen minutes a white precipitate began to form. The mixture was stirred an additional hour and filtered. The solid was dried under vacuum at room temperature. Anal. Calcd. for KZn_2H_5: K, 22.4; Zn, 74.8; H, 2.88. Found: K, 23.2; Zn, 74.0; H, 2.79. The molar ratio of K:Zn:CH_3:H was 1.05:2.00:0.00:4.92. The filtrate contained 10.21 mmoles of aluminum, no zinc and 5.26 mmoles of potassium. The molar ratio of K:Al in the filtrate was 1.03:2.00. The X-ray powder diffraction pattern of the solid is given in Table 2.

Preparation of KZn_2H_5 by Reaction of AlH_3 with $KZn_2(CH_3)_4H$ in Tetrahydrofuran. 20 mmoles of dimethylzinc in tetrahydrofuran was added to 10 mmoles of KH slurried in tetrahydrofuran. A clear solution resulted even before all the dimethylzinc could be introduced. The solution was quickly cooled to -80° and stirred for an additional hour at this temperature. Next, 14.82 mmoles of AlH_3 in tetrahydrofuran was added to the solution, which was still at -80°. A faint white precipitate appeared immediately. The bath was removed and the mixture stirred for one hour,

then filtered. The solid was dried under vacuum at room temperature. Anal. Calcd. for KZn_2H_5: K, 22.4; Zn, 74.8; H, 2.88. Found: K, 21.5; Zn, 75.8; H, 2.79. The molar ratio of K:Zn:H was 1.00:2.10:5.04. The filtrate contained 16.96 mmoles of aluminum, no zinc, and 0.83 mmoles of potassium. The molar ratio of K:Al in the filtrate was 0.098:2.00. The X-ray powder diffraction pattern of the solid is given in Table 2.

Attempted Preparation of KZn_3H_7 by Reaction of AlH_3 with $KZn_3(CH_3)_6H$ in Tetrahydrofuran. 15 mmoles of dimethylzinc in tetrahydrofuran was added to 5 mmoles of KH slurried in tetrahydrofuran. The clear solution which resulted was cooled to -80° and stirred for one hour. Next, 15 mmoles of AlH_3 in tetrahydrofuran was added to the solution, which was still at -80°. The mixture was allowed to warm to room temperature (a white precipitate formed in the process), stirred for one hour, then filtered. The solid was dried under vacuum at room temperature. Anal. Calcd. for KZn_3H_7: K, 16.1; Zn, 80.9; H, 2.92. Found: K, 15.0; Zn, 82.1; H, 2.92. The molar ratio of K:Zn:H was 1.00:3.29:7.56. The filtrate contained 16.09 mmoles of aluminum, no zinc, and 0.44 mmoles of potassium. The molar ratio of K:Al in the filtrate was 0.055:2.00. The X-ray diffraction pattern of the solid, which is given in Table 2, showed lines due to KZn_2H_5 only.

Preparation of $KZnH_3$ by Reacting $LiAlH_4$ with $KZn(CH_3)_2H$ in Tetrahydrofuran. 10 mmoles of dimethylzinc in tetrahydrofuran was added to 10 mmoles of KH slurried in tetrahydrofuran. The clear solution which resulted was cooled to -80° and stirred for one hour. Next 10 mmoles of lithium aluminum hydride in tetrahydrofuran was added to the solution.

The solution was warmed to room temperature and a white precipitate resulted. This mixture was stirred for one hour and filtered. The resulting white solid was dried under vacuum at room temperature. Anal. Calcd. for $KZnH_3$: K, 36.4; Zn, 60.8; H, 2.81. Found: K, 36.6; Zn, 60.5; H, 2.86. The molar ratio of Li:K:Zn:H was 0.00:1.01:1.00:2.96. The filtrate contained 9.64 mmoles of aluminum, no zinc, no potassium, and 9.75 mmoles of lithium. The molar ratio of K:Li:Al in the filtrate was 0.00:1.01:1.00. The X-ray powder diffraction pattern of the solid is given in Table 2.

Preparation of $NaZnH_3$ by Reaction of $NaAlH_4$ with $NaZn(CH_3)_2$ in Tetrahydrofuran. 10 mmoles of dimethylzinc in tetrahydrofuran was added to 10 mmoles of NaH slurried in tetrahydrofuran. The mixture was quickly cooled to -80° and stirred at that temperature until the Na:Zn ratio in the supernatant was 1:1. At this point, 5 mmoles of the supernatant [$NaZn(CH_3)_2H$ solution] was allowed to react with 5 mmoles of sodium aluminum hydride in tetrahydrofuran. A white precipitate appeared within minutes. The mixture was stirred twenty minutes and filtered. The resulting white solid was dried under vacuum at room temperature. Anal. Calcd. for $NaZnH_3$: Na, 25.2; Zn, 71.5; H, 3.30. Found: Na, 25.2; Zn, 71.6; H, 3.24. The molar ratio of Na:Zn:H was 1.00:1.00:2.94. The X-ray powder diffraction pattern is given in Table 3. The filtrate contained 4.62 mmoles of aluminum, 0.47 mmoles of zinc, and 5.06 mmoles of sodium.

Attempted Preparation of $NaZn_2H_5$ by Reaction of $NaAlH_4$ with $NaZn_2(CH_3)_4H$ in Tetrahydrofuran. 20 mmoles of dimethylzinc in tetrahydrofuran were added to 10 mmoles of NaH slurried in tetrahydrofuran. The

mixture was quickly cooled to -80° and stirred until the Na:Zn ratio in the supernatant was 0.50:1.00. At this point, 5 mmoles of the supernatant [$NaZn_2(CH_3)_4H$ solution] was allowed to react with 10 mmoles of sodium aluminum hydride in tetrahydrofuran. A white precipitate appeared within minutes. The mixture was stirred for an hour and filtered. The resulting white solid was dried at room temperature under vacuum. The molar ratio of Na:Zn:H in the solid was 1.00:1.00:2.90. The X-ray powder diffraction pattern, given in Table 3, was identical to that for $NaZnH_3$. The filtrate contained 10.00 mmoles of aluminum, 3.06 mmoles of zinc, and 9.50 mmoles of sodium.

Results and Discussion

While there have been many cases,[3,7,8] of the preparation of simple metal hydrides of the main group elements by the reduction of a metal alkyl with lithium aluminum hydride,[9] no one has applied this simple reaction to the synthesis of new complex metal hydrides. Over the past twenty years, many new "ate" complexes have been reported[4,10,11] which conceivably could

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be reduced to the corresponding complex metal hydride by reduction of the alkyl with lithium aluminum hydride. When we discovered that the "ate" complexes of zinc are cleaved by ether solvents, at the temperatures necessary to carry out hydrogenolysis (75-150°) to the corresponding hydride, it was necessary to develop another method of reduction that could be carried out at lower temperatures. It was found that $LiAlH_4$, $NaAlH_4$, or AlH_3 will reduce the "ate" complex to the corresponding hydride rapidly at room temperature.

$$MH + ZnR_2 \longrightarrow MZnR_2H \xrightarrow[75\text{-}150^\circ]{H_2} MZnH_3 + \text{other cleavage products}$$

$$MZnR_2H \xrightarrow{LiAlH_4} MZnH_3 + LiAlR_2H_2$$

Li_2ZnH_4. The "ate" complex $Li_2Zn(CH_3)_4$, lithium tetramethylzincate, first prepared by Hurd[12] in 1948, has been characterized both by NMR, [11d]

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(12) D. J. Hurd, J. Org. Chem., 13, 711 (1948).

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and X-ray crystallography.[13] Its structure is shown below.

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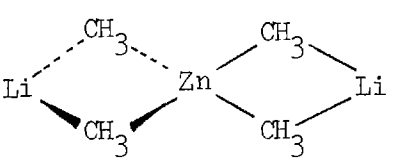
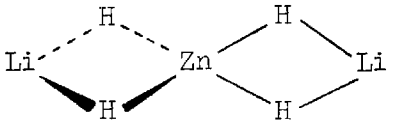
(13) E. Weiss and R. Wolfrum, Chem. Ber., 101, 35 (1968).



Thus, the reaction of $LiAlH_4$ with $Li_2Zn(CH_3)_4$ should serve as a convenient route to Li_2ZnH_4 (eq. 1).

$$Li_2Zn(CH_3)_4 + 2\ LiAlH_4 \longrightarrow Li_2ZnH_4 + 2\ LiAl(CH_3)_2H_2 \qquad (1)$$

When $Li_2Zn(CH_3)_4$ and $LiAlH_4$ were allowed to react, Li_2ZnH_4 was obtained in 100% yield. The X-ray powder diffraction pattern of Li_2ZnH_4 (Table 1) contained no lines due to LiH or ZnH_2, therefore, the product is not a physical mixture of the two simple hydrides. On the other hand, the powder diffraction pattern was similar to that found for K_2ZnH_4 (Table 2). Also, the infrared spectrum of Li_2ZnH_4 was similar to the spectrum of K_2ZnH_4. The infrared spectrum of the solution that remained after filtration of Li_2ZnH_4 showed that the aluminum containing species was $LiAl(CH_3)_2H_2$. Therefore, complete exchange of the methyl groups from zinc to aluminum had occurred. The structure of Li_2ZnH_4 might be similar to that of $Li_2Zn(CH_3)_4$, however, due to the insolubility of the hydride, association, ir, and nmr data is not available to establish this point.



Oddly enough, the reaction of either $LiZn(s\text{-}C_4H_9)_2H$, $LiZn(CH_3)_2H$, or $LiZn_2(CH_3)_4H$ with $LiAlH_4$ in tetrahydrofuran yields Li_2ZnH_4. The X-ray powder diffraction patterns of Li_2ZnH_4 from each of these reactions (Table 1) show weak to moderate lines for Li_2ZnH_4 and strong lines for zinc metal. The zinc metal undoubtedly comes from thermal decomposition of Li_2ZnH_4 at room temperature, a reaction which occurs slowly in all samples of Li_2ZnH_4. Li_2ZnH_4 prepared from $Li_2Zn(CH_3)_4$ showed no zinc metal

lines since it was only stirred in the reaction mixture for about one hour before filtration.

$$LiZnR_2H + LiAlH_4 \longrightarrow Li_2ZnH_4 + Zn + H_2 + LiAlR_2H_2$$

Li_2ZnH_4 from the above three reactions was stirred in tetrahydrofuran for about 24 hours. The presence of large excess of tetrahydrofuran with any of the complex metal hydrides discussed here always greatly increased the rate of decomposition to zinc metal at room temperature. After this trend had been noticed, all solid products were filtered as quickly as possible in order to keep them pure.

The route by which Li_2ZnH_4 is formed from $LiZn(s\text{-}C_4H_9)_2H$, $LiZn(CH_3)_2H$, or $LiZn_2(CH_3)_4$ is not clear, especially in the case of $LiZn_2(CH_3)_4H$. A reasonable explanation for the formation of Li_2ZnH_4 from $LiZn(s\text{-}C_4H_9)_2H$ or $LiZn(CH_3)_2H$ is that $LiAlH_4$ exchanges its hydrido groups for the alkyl groups on zinc in a stepwise fashion. After the first alkyl exchange step, $LiZnRH_2$ (where R = CH_3 or $s\text{-}C_4H_9$) would be formed which could then disproportionate to Li_2ZnH_4 and ZnR_2 faster than the reaction with $LiAlRH_3$ (eq. 2).

$$2\ LiZn(CH_3)H_2 \longrightarrow Li_2ZnH_4 + (CH_3)_2Zn \qquad (2)$$

This explanation is supported by elemental analysis of the reaction mixtures from reduction of $LiZn(s\text{-}C_4H_9)_2H$ and $LiZn(CH_3)_2H$ with $LiAlH_4$. The solid product from the reaction of $LiZn(s\text{-}C_4H_9)_2H$ with $LiAlH_4$ had a molar ratio of Li:Zn:H of 2:1:4. The filtrate contained one-half of the starting zinc. Thus the solid, Li_2ZnH_4, contained the other half. This is consistent with the disproportionation of an intermediate complex to equimolar

amounts of di-s-butylzinc and Li_2ZnH_4. Evidently, di-s-butylzinc was not reduced to zinc hydride by the intermediate aluminum hydride species, $LiAl(s\text{-}C_4H_9)H_3$. The solid from the reaction of $LiZn(CH_3)_2H$ with $LiAlH_4$ had a molar ratio of Li:Zn:H of 1:1:3. The filtrate contained very little of the starting zinc compound and the X-ray powder diffraction pattern showed only lines for Li_2ZnH_4 and zinc metal. Thus, the solid product must be a mixture of Li_2ZnH_4 and ZnH_2, where the ZnH_2 comes from reduction of $(CH_3)_2Zn$ with $LiAl(CH_3)H_3$. A situation similar to this was encountered by Coates[14] in the preparation of $LiBeH_3$. The X-ray powder diffraction

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(14) N. A. Bell and G. E. Coates, J. Chem. Soc., A, 628 (1968).

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pattern of the compound contained lines due to Li_2BeH_4 only, but the analysis showed a molar ratio of Li:Be:H of 1:1:3. Coates concluded that the product was an equimolar mixture of Li_2BeH_4 and BeH_2.

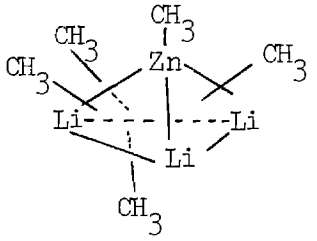
The analysis of the reaction mixtures from the reduction of $LiZn_2(CH_3)_4H$ with $LiAlH_4$ showed no simple trends. Thus, a mechanism for the formation of Li_2ZnH_4 by this reaction will not be offered.

Li_3ZnH_5. In their low temperature NMR work on the system CH_3Li-$(CH_3)_2Zn$, Seitz and Brown[11d] reported the existence of two complexes, $Li_2Zn(CH_3)_4$ and $Li_3Zn(CH_3)_5$. Since reduction of $Li_2Zn(CH_3)_4$ with $LiAlH_4$ yields Li_2ZnH_4, reduction of $Li_3Zn(CH_3)_5$ with $LiAlH_4$ should be a convenient route to Li_3ZnH_5 (eq. 3).

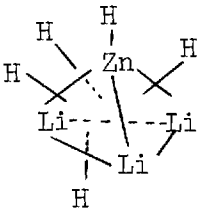
$$Li_3Zn(CH_3)_5 + 5/2\ LiAlH_4 \longrightarrow Li_3ZnH_5 + 5/2\ LiAl(CH_3)_2H_2 \quad (3)$$

The reaction of $Li_3Zn(CH_3)_5$ with $LiAlH_4$ in diethyl ether at room temperature gave Li_3ZnH_5, in 100% yield. The product contained a small

amount of $LiAlH_4$ which precipitated with the product. The X-ray powder diffraction pattern (Table 1) did not contain any lines due to Li_2ZnH_4, ZnH_2, or LiH. Therefore, Li_3ZnH_3 is a true compound not a physical mixture. The infrared spectrum of Li_3ZnH_5 had two strong and two moderate bands. The two strong bands are centered at 680 cm^{-1} and 1550 cm^{-1}. The two moderate bands are centered at 990 cm^{-1} and 1280 cm^{-1}. The structure of Li_3ZnH_5 is believed to be the same as that proposed by Seitz and Brown[11d] for $Li_3Zn(CH_3)_5$.



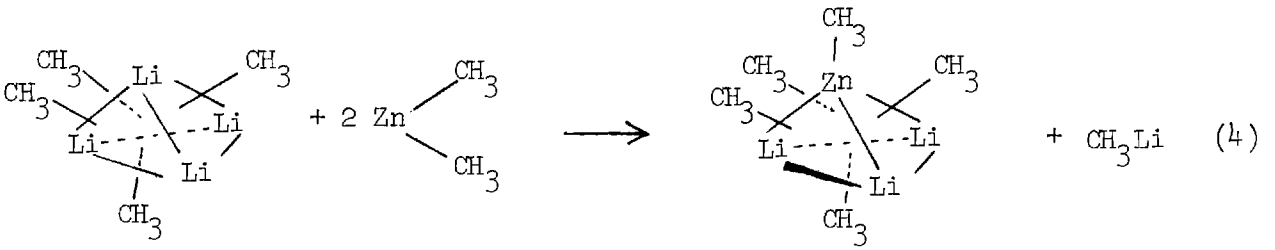
$Li_3Zn(CH_3)_5$



(Li_3ZnH_5)

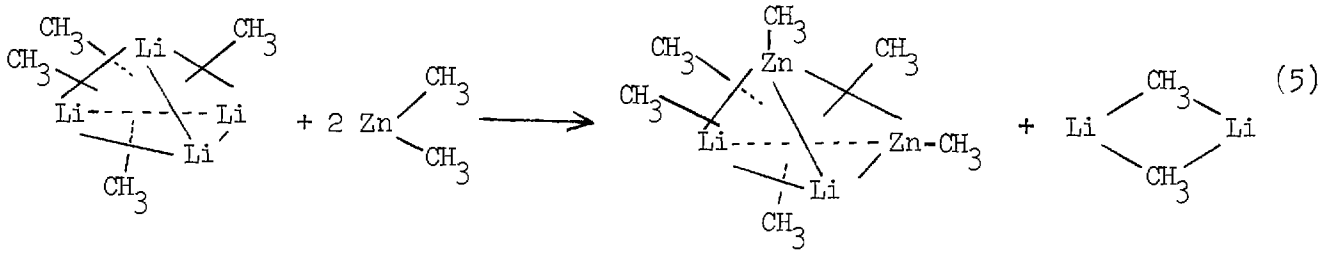
Once again due to the insolubility of the product, it was not possible to determine the structure by the usual methods (association, nmr and ir).

<u>$LiZnH_3$</u>. $Li_3Zn(CH_3)_5$ has been reported [11d] to be formed in diethyl ether by substitution of one dimethylzinc molecule for one methyl lithium molecule in the methyl lithium tetramer (eq. 4).



(4)

$LiZn(CH_3)_3$ could then be formed by substitution of two dimethylzinc molecules for two methyl lithium molecules in the methyl lithium tetramer in diethyl ether solution (eq. 5).



(5)

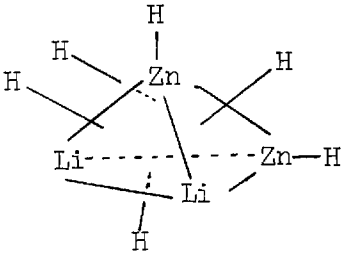
$LiZn(CH_3)_3$ formed in this way should provide an excellent precursor to $LiZnH_3$.

The reaction of a 1:1 mixture of methyllithium and dimethylzinc with $LiAlH_4$ in diethyl ether gave $LiZnH_3$ (eq. 6). The X-ray powder

$$1/2\ (LiCH_3)_4 + 2\ Zn(CH_3)_2 \longrightarrow Li_2Zn_2(CH_3)_6$$

$$1/2\ Li_2Zn_2(CH_3)_6 + 3/2\ LiAlH_4 \longrightarrow LiZnH_3 + 3/2\ LiAl(CH_3)_2H_2 \qquad (6)$$

diffraction pattern of $LiZnH_3$ (Table 1) was very different from those of Li_2ZnH_5 or Li_3ZnH_5 and did not contain any lines for LiH or ZnH_2. $LiZnH_3$ is believed to have the structure shown below.



$\underline{LiZn_2H_5 \text{ and } LiZn_3H_6}$. 1:2 and 1:3 mixtures of methyllithium and dimethylzinc were allowed to react with $LiAlH_4$ in diethyl ether. The solid compounds obtained had Li:Zn:H ratios of 1:2:5 and 1:3:7. However, the X-ray powder diffraction patterns of the solids (Table 1) contained lines due only to $LiZnH_3$. Thus, the solid compounds are 1:1 and 1:2 mixtures of $LiZnH_3$ and ZnH_2.

$\underline{KZn(CH_3)_2H \text{ and } KZn_2(CH_3)_2H}$. Contrary to the reaction of di-s-butylzinc with KH, which yields K_2ZnH_4 directly, KH and dimethylzinc were found to give the 1:1 complex potassium dimethylhydridozincate in quantitative yield when the reaction is carried out in diethyl ether or tetrahydrofuran. This complex had not been prepared previously, however, its properties were found to be analogous to those of $LiZn(CH_3)_2H$ and $NaZn(CH_3)_2H$ which had been prepared earlier by Shriver[4]. Like the lithium and sodium complexes, $KZn(CH_3)_2H$ was insoluble in diethyl ether, but soluble in tetrahydrofuran. $KZn(CH_3)_2H$ was found to react with another molecule of $(CH_3)_2Zn$ to give $KZn_2(CH_3)_4H$, which like the lithium and sodium complexes decomposed to $KZn(CH_3)_2H$ and $(CH_3)_2Zn$ when an attempt was made to isolate them as solids under vacuum.

$\underline{KZn_2H_5}$. The reaction of $KZn(CH_3)_2H$ with AlH_3 in tetrahydrofuran (AlH_3 was chosen as reducing agent for fear of alkali metal exchange if $LiAlH_4$ were used) was selected as a convenient route to $KZnH_3$. However, the reaction readily proceeds to give KZn_2H_2 (eq. 7) in quantitative yield.

$$2\ KZn(CH_3)_2H + 2\ AlH_3 \longrightarrow KZn_2H_5 + KAl_2(CH_3)_4H_3 \qquad (7)$$

The X-ray powder diffraction pattern for KZn_2H_5 (Table 2) contains no

lines due to KH, ZnH_2, or K_2ZnH_4. The aluminum containing species remaining after precipitation of KZn_2H_5 is at present unknown. The species shown in eq. 7 seems reasonable but proof of its existence is yet to be obtained.

KZn_2H_5 was also formed by reduction of $KZn_2(CH_3)_4$ with AlH_3 in tetrahydrofuran (eq. 8).

$$KZn(CH_3)_4H + 2\ AlH_3 \longrightarrow KZn_2H_5 + 2\ Al(CH_3)_2H \qquad (8)$$

In this reaction very little potassium was found in the filtrate. The X-ray powder diffraction pattern of KZn_2H_5 obtained from this reaction is shown in Table 2. The structure of KZn_2H_5 is at present unknown.

$\underline{KZn_3H_7}$. Reaction of a 1:3 mixture of KH and $(CH_3)_2Zn$ with AlH_3 in tetrahydrofuran gave a white solid with K:Zn:H ratio of 1:3:7, however, the X-ray powder diffraction pattern showed only lines for KZn_2H_5. Thus, the compound must be a 1:1 mixture of KZn_2H_5 and ZnH_2.

$\underline{KZnH_3}$. The reaction of $KZn(CH_3)_2H$ with $LiAlH_4$ in tetrahydrofuran gave $KZnH_3$ (no alkali metal exchange) in quantitative yield (eq. 9).

$$KZn(CH_3)_2H + LiAlH_4 \longrightarrow KZnH_3 + LiAl(CH_3)_2H_2 \qquad (9)$$

The X-ray powder diffraction pattern of $KZnH_3$ (Table 2) did not contain any lines due to KZn_2H_5, K_2ZnH_4, ZnH_2, or KH. The structure of $KZnH_3$ is at the present unknown.

$\underline{NaZnH_3}$. The reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in tetrahydrofuran gave $NaZnH_3$ (eq. 10). The X-ray powder diffraction pattern (Table 3) was

$$NaZn(CH_3)_2H + NaAlH_4 \longrightarrow NaZnH_3 + NaAl(CH_3)_2H_2 \qquad (10)$$

identical to that reported by Shriver[7] in his preparation of $NaZnH_3$. [Shriver's preparation involved a thermal decomposition of $NaZn_2(CH_3)_2H_3$ under vacuum to give $NaZnH_3$ and $(CH_3)_2Zn$.] Vacuum DTA-TGA analysis of $NaZnH_3$ showed a strong exotherm at 72° and moderate endotherm at 104, 183 and 250°. The simultaneous weight loss curve showed inflections that corresponded to equivalent weight losses at each of the endotherms and no weight loss at the exotherm. The first endotherm corresponded to the thermal decomposition of ZnH_2. The exotherm can then be attributed to disproportionation of $NaZnH_3$ to Na_2ZnH_4 and ZnH_2. Therefore, Na_2ZnH_4 is more thermodynamically stable than $NaZnH_3$, thus explaining why $NaZnH_3$ turns black on standing at room temperature. (A phenomenon reported by Shriver[7] and observed by the author.) Thermal decomposition of $NaZnH_3$ can be envisioned as proceeding by the following steps.

$$2\ NaZnH_3 \longrightarrow Na_2ZnH_4 + ZnH_2 \qquad (1)$$

$$ZnH_2 \longrightarrow Zn + H_2 \qquad (2)$$

$$Na_2ZnH_4 \longrightarrow 2\ NaH + Zn + H_2 \qquad (3)$$

$$2\ NaH \longrightarrow 2\ Na + H_2 \qquad (4)$$

The endotherm at 250° corresponds to thermal decomposition of NaH. The DTA-TGA reported previously by R. G. Beach for Na_2ZnH_4 was different than the one reported here. But a difference should be expected since his DTA-TGA was run under argon at one atmosphere pressure and the DTA-TGA reported here was carried out under vacuum.

The reaction of $NaZn_2(CH_3)_4H$ with $NaAlH_4$ also yielded $NaZnH_3$. The X-ray powder diffraction pattern of $NaZnH_3$ prepared by this route

is given in Table 3. The mechanism by which $NaZnH_3$ was formed in this reaction is not understood at present.

The reduction of "ate" complexes with $LiAlH_4$, $NaAlH_4$, or AlH_3 to give complex metal hydrides appears to be a very general reaction of unlimited applicability. Seemingly, if one desires to prepare a certain complex metal hydride, all that is needed is the selection of the proper "ate" complex and reduction of the complex with $LiAlH_4$, $NaAlH_4$, or AlH_3 will yield the hydride. To date five new complex metal hydrides of zinc have been prepared using this procedure. Vacuum DTA-TGA analysis of these hydrides is in progress. We feel that our goal of a complete spectrum of complex metal hydrides of zinc with lithium, sodium, and potassium will be complete in the very near future. Indeed, $LiZn_2H_5$, $NaZn_2H_5$, and Na_2ZnH_4 are the only ones lacking. The reaction of AlH_3 with $LiZn(CH_3)_2H$ and $NaZn(CH_3)_2H$ should yield $LiZn_2H_5$ and $NaZn_2H_5$, as it did with $KZn(CH_3)_2H$.

Acknowledgment. We are indebted to the Office of Naval Research (Contract No. N000 14-67-A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

Table 1. X-Ray Powder Patterns For Complex Metal Zinc Hydrides of Lithium

Li_2ZnH_4 + Zn[a]		Li_2ZnH_4 + Zn[b]		Li_2ZnH_4 + Zn[c]		Li_2ZnH_4[d]	
d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$
4.25	m	4.25	m	4.22	mw	5.02	m
3.83	m	3.85	m	3.85	w	4.69	w
3.67	w	3.69	mw	3.69	w	4.25	s
3.44	m	3.44	m	3.42	w	3.84	vs
2.95	m	2.95	m	3.25	vw	3.65	m
2.70	w	2.68	mw	2.95	mw	3.42	ms
2.47	m	2.46	ms	2.73	w	2.95	ms
2.43	m	2.29	ms	2.46	ms	2.71	mw
2.29	w	2.09	vs	2.29	ms	2.46	s
2.12	w	1.90	vw	2.09	s	2.42	s
2.08	m	1.83	vw	1.68	m	2.32	m
1.95	w	1.68	m	1.34	m	2.26	mw
1.84	w	1.33	m	1.33	m	2.24	mw
1.68	w	1.23	w	1.23	w	2.12	m
1.60	w	1.17	m	1.17	m	2.07	w
1.17	w	1.15	w	1.15	w	1.99	m
0.90	w	1.12	m	1.12	m	1.91	m
0.865	w	1.09	w	1.09	w	1.84	m
		1.04	w	1.04	w	1.79	m
		0.941	w	0.941	w	1.70	w
		0.907	w	0.907	w	1.67	w
		0.904	w	0.905	w	1.64	w
		0.903	w	0.87	w	1.60	m
		0.870	w	0.856	w	1.57	w
		0.856	w	0.855	w	1.54	w
		0.854	w	0.821	w	1.52	w
		0.821	w	0.819	w	1.50	w
		0.818	w			1.48	m
						1.47	m
						1.456	w
						1.44	w
						1.397	w
						1.36	w
						1.34	w
						1.32	w
						1.29	w
						1.21	w

[a] $LiZn(s\text{-}C_4H_9)_2H + LiAlH_4$ in THF. [b] $LiZn(CH_3)_2H + LiAlH_4$ in THF.

[c] $LiZn_2(CH_3)_4H + LiAlH_4$ in THF. [d] $Li_2Zn(CH_3)_4 + LiAlH_4$ in diethyl ether.

[e] $Li_3Zn(CH_3)_5 + LiAlH_4$ in diethyl ehter.

Table 1 (Continued)

Li_3ZnH_5[e] d,A	I/I$_o$	$LiZnH_3$[f] d,A	I/I$_o$	"$LiZn_2H_5$"[g] d,A	I/I$_o$	"$LiZn_3H_7$" + Zn[h] d,A	I/I$_o$
4.45	w	6.25	m	6.24	m	6.24	m
2.84	s	5.02	w	4.45	s	4.45	s
2.78	w	4.45	vs	4.30	m	3.24	m
2.64	m	4.30	m	3.26	s	3.10	m
2.50	m	4.19	m	3.10	m	2.91	mw
1.91	w	3.81	ms	2.94	m	2.81	m
1.79	w	3.65	w	2.81	m	2.45	m
1.63	ms	3.42	mw	2.50	m	2.31	mw
1.50	m	3.24	vs	2.41	m	2.16	mw
1.385	w	3.10	m	2.24	w	2.09	s
		2.94	s	2.17	mw	1.98	w
		2.81	s	2.07	w	1.96	w
		2.50	mw	1.98	w	1.75	w
		2.45	m	1.95	w	1.68	w
		2.41	m	1.75	w	1.33	w
		2.31	w	1.60	w	1.17	w
		2.24	mw	1.495	w	1.12	w
		2.16	mw	1.25	vw		
		2.12	w				
		2.06	w				
		1.98	mw				
		1.94	mw				
		1.90	mw				
		1.84	w				
		1.75	mw				
		1.64	w				
		1.60	m				
		1.52	w				
		1.495	w				
		1.44	w				
		1.244	w				

[f] $LiZn(CH_3)_3$ + $LiAlH_4$ in diethyl ether. [g] $LiZn_2(CH_3)_5$ + $LiAlH_4$ in diethyl ether. [h] $LiZn_3(CH_3)_7$ + $LiAlH_4$ in diethyl ether. [i] ASTM File. [j] ASTM File.

[k] $LiAlH_4$ – $(C_2H_5)_2Zn$, see ref. 3.

Table 1 (Continued)

Zn[i] d,A	I/I$_o$	LiH[j] d,A	I/I$_o$	ZnH_2[k] d,A	I/I$_o$
				4.51	vw
				4.23	s
				3.80	vw
				3.40	m
				2.97	vw
				2.828	vw
2.473	m			2.608	w
		2.357	m	2.468	vw
2.308	m			2.387	m
				2.290	m
2.091	s			2.225	m
		2.041	s	2.135	w
				2.085	w
				2.017	vw
1.687	m			1.905	w
				1.764	w
		1.444	m	1.688	vw
1.342	m			1.603	vw
1.332	m			1.562	vw
1.237	w	1.231	mw	1.486	vw
1.173	m	1.178	w	1.464	vw
1.154	w			1.416	vw
1.124	w			1.336	vw
1.091	w			1.305	vw
1.046	w			1.295	vw
		1.020	vw	1.259	vw
		0.9374	w	1.219	vw
		0.9130	w	1.172	vw
		0.8335	w	1.157	vw
		0.7859	vw	1.123	vw
				1.042	vw

w, weak; m, medium; s, strong; v, very

Table 2. X-Ray Powder Patterns For Complex Metal Zinc Hydrides of Potassium

$KZn(CH_3)_2 + KH$[a]		KH[b]		K_2ZnH_4[c]		ZnH_2[d]		KZn_2H_5[e]	
d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$
6.10	mw			5.10	w	4.51	vw	6.03	s
5.30	mw			4.26	m	4.23	s	4.10	mw
4.05	mw,d			3.89	w	3.80	vw	3.72	mw
3.89	mw,d			3.62	vw	3.40	m	3.36	vs
3.59	ms,d			3.47	m	2.97	vw	3.01	m
3.40	ms,d			3.24	w	2.828	vw	2.67	vw
3.27	s	3.30	vs	3.09	s	2.608	w	2.59	vw
2.83	s	2.86	s	2.940	s	2.468	vw	2.42	s
2.75	w			2.744	w	2.387	m	2.35	s
2.45	m			2.568	vvw	2.290	m	2.18	m
2.10	w			2.354	w	2.225	m	2.14	vw
2.00	ms	2.02	s	2.128	w	2.135	w	2.00	vw
1.71	ms	1.72	s	1.946	w	2.085	w	1.93	ms
1.64	w	1.65	m	1.814	w	2.017	vw	1.85	m
1.57	vw			1.734	w	1.905	w	1.80	m
1.43	w	1.43	m	1.648	vw	1.764	w	1.68	m
1.30	w	1.31	m	1.624	vw	1.688	vw	1.54	w
1.27	w	1.28	m	1.571	w	1.630	vw	1.49	m
1.16	w	1.17	m	1.488	w	1.562	vw	1.431	w
1.09	w	1.10	m	1.470	w	1.486	vw	1.414	w
0.96	w	1.01	w	1.384	vw	1.464	vw	1.371	mw
				1.213	w	1.416	vw	1.355	mw
						1.336	vw	1.328	w
						1.305	vw	1.269	vw
						1.295	vw	1.238	vw
						1.219	vw	1.222	w
						1.172	vw	1.176	w
						1.157	vw	1.151	vw
						1.123	vw	1.111	w
						1.042	vw	1.076	vw
								1.060	vw
								1.005	vw
								0.983	vw
								0.922	vw
								0.888	vw

[a] Excess KH + $(CH_3)_2Zn$ in diethyl ether. [b] ASTM Files

[c] KH + $(s\text{-}C_4H_9)_2Zn$ in benzene, see ref. 3. [d] $LiAlH_4$ + $(C_2H_5)_2Zn$, see ref. 3.

[e] $KZn(CH_3)_2H + AlH_3$ in tetrahydrofuran. [f] $KZn_2(CH_3)_4H + AlH_3$ in tetrahydrofuran.

Table 2 (Continued)

KZn_2H_5[f]		"KZn_3H_7"[g]		$KZnH_3$[h]	
d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$
6.03	s	6.02	ms	6.25	ms
4.08	mw	4.06	mw	5.60	vw
3.72	w	3.72	w	5.10	s
3.36	vs	3.36	vw	4.40	vw
3.02	mw	3.02	mw	3.71	vw
2.69	w	2.79	vw	3.59	m
2.61	w	2.69	vw	3.43	vs
2.43	s	2.60	vw	3.31	m
2.34	s	2.43	s	3.11	ms
2.18	m	2.35	s	2.80	s
2.02	w	2.28	vw	2.71	vs
1.93	ms	2.19	m	2.58	s
1.85	m	2.09	m	2.33	s
1.80	m	2.03	vw	2.29	w
1.68	m	2.01	vw	2.18	w
1.53	w	1.93	ms	2.15	vw
1.490	m	1.86	m	2.12	vw
1.432	w	1.81	m	2.07	m
1.415	w	1.69	m	2.03	w
1.371	w	1.65	vw	1.94	vw
1.351	w	1.53	vw	1.90	ms
1.322	w	1.49	m	1.86	w
1.270	w	1.435	mw	1.85	vw
1.234	vw	1.419	w	1.79	m
1.222	w	1.361	mw	1.77	m
1.191	vw	1.355	mw	1.73	m
1.175	w	1.321	vw	1.72	w
1.154	vw	1.300	vw	1.69	m
1.111	w	1.271	vvw	1.66	w
1.078	w	1.239	vvw	1.64	w
1.057	w	1.223	w	1.595	m
1.003	vw	1.221	vw	1.57	w
0.986	vw	1.175	vw	1.55	w
0.922	vw	1.152	vw	1.455	mw
0.906	vw	1.111	w	1.370	mw
		1.079	w	1.325	mw
		1.059	w		

[g] $KZn_3(CH_3)_6 + AlH_3$ in tetrahydrofuran. [h] $KZn(CH_3)_2H + LiAlH_4$ in tetrahydrofuran.

w, weak; m, medium; s, strong; v, very; d, diffused.

Table 3. X-Ray Powder Patterns for Complex Metal Zinc Hydrides of Sodium

$NaZnH_3$[a]		$NaZnH_3$[b]		$NaZnH_3$[c]		NaH[d]	
d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$	d,A	I/I$_o$
8.70	vw	8.70	vw				
5.99	w	5.99	w	5.87	vw		
4.90	vs	4.90	vs	4.90	s		
4.39	w	4.40	w				
3.98	w	3.91	w				
3.30	m	3.52	w				
3.11	vs	3.27	ms	3.26	m		
2.91	m	3.11	vs	3.11	vs		
2.81	w	2.92	m				
2.63	mw	2.81	m	2.84	w	2.83	s
2.56	m	2.62	w				
2.49	ms	2.56	ms				
2.43	m	2.49	s	2.51	m	2.44	ms
2.38	vw	2.44	m	2.45	w		
2.26	w	2.25	w	2.38	vw		
2.22	w	2.20	w	2.28	vw		
2.15	w	2.15	vw	2.23	vw		
2.07	w	2.07	w	2.16	vvw		
1.96	mw	2.02	vw	2.09	vw		
1.83	mw	1.97	mw	2.02	vvw		
1.78	w	1.84	w	1.98	w		
1.72	vw	1.78	w	1.79	vvw	1.73	ms
1.66	mw	1.70	w	1.70	vvw	1.47	ms
1.61	mw	1.66	w	1.67	vw	1.41	m
1.58	vw	1.61	mw	1.62	w	1.22	mw
1.53	mw	1.58	w	1.55	w	1.12	m
1.49	vw	1.53	mw	1.47	vvw	1.09	m
1.38	vw	1.49	vw	1.35	vw	0.996	m
1.34	w	1.47	vw			0.939	m
1.22	vw	1.37	vw			0.863	mw
1.06	vw	1.34	vw			0.825	m
1.00	vw	1.22	vw			0.813	m
		1.00	vvw				

[a] $NaZn(CH_3)_2H + NaAlH_4$ in tetrahydrofuran. [b] $NaZn_2(CH_3)_4H + NaAlH_4$ in tetrahydrofuran. [c] See ref. 7, made by thermally decomposing $NaZn_2(CH_3)_2H_3$.

[d] ASTM File. w, weak; m, medium; s, strong; v, very.

Synthesis of Complex Metal Hydrides of Copper

E. C. Ashby and T. F. Korenowski

Abstract

The first complex metal hydrides of Copper, $LiCuH_2$ and Li_3CuH_4 have been prepared by reaction of $LiAlH_4$ with $LiCu(CH_3)_2$ and $Li_3Cu(CH_3)_4$. The compounds were not obtained in as pure a state as we hope to get them after further work. The new hydrides are very air sensitive.

Introduction

Copper hydride, of the approximate composition CuH, was first prepared by Wurtz in 1844 by the reduction of copper sulphate with hypophosphorous acid in aqueous solution.[1] This often impure reddish-brown material has been found to be thermodynamically unstable[2] and insoluble in nondestructive solvents. More recently, Wiberg and Henle[3] reported that copper hydride prepared by reaction of copper (I) iodide with $LiAlH_4$ was soluble in coordinating organic solvents.

This novel form of CuH was more fully characterized by Dilts and Shriver.[4] They also effectively demonstrated that its solubility

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(1) A. Wurtz, Ann. Chim. Phys., 11, 250 (1844).

(2) J. C. Warf, J. Inorg. Nucl. Chem., 19, 304 (1961).

(3) E. Wiberg and W. Henle, Z. Naturforsch., 7b, 250 (1952).

(4) J. A. Dilts and D. F. Shriver, J. Amer. Chem. Soc., 90, 5796 (1968).

was due to the formation of copper hydride complexes with Lewis bases.[5]

(5) J. A. Dilts and D. F. Shriver, J. Amer. Chem. Soc., 91, 4088 (1969).

This reported ability of copper hydride to undergo complex formation suggested to us that it should be possible to synthesize complex metal hydrides of copper which should be much more stable than CuH. In addition, complex metal hydrides of copper should be potentially excellent burning rate accelerators and reducing agents. Therefore, as a first possibility, we sought to prepare $LiCuH_2$ by metathesis of $LiCu(CH_3)_2$ and $LiAlH_4$ as described by reaction (1).

$$LiCu(CH_3)_2 + LiAlH_4 \xrightarrow{Et_2O} LiCuH_2 + LiAlH_2(CH_3)_2 \qquad (1)$$

Experimental

Equipment and Materials. All manipulations of solvents and compounds were performed under an atmosphere of purified nitrogen by the use of Schlenk type apparatus and dry box techniques. Diethyl ether was purified by distillation from $LiAlH_4$ and used immediately. Copper (I) iodide, obtained from Fisher Scientific Company, was purified by reported procedures.[4] Lithium aluminum hydride was obtained from Alpha Inorganics Inc. and used as standarized solutions in diethyl ether. Halide free diethyl ether solutions of methyl lithium were used as obtained from Matheson Coleman and Bell. Infrared spectral

measurements were obtained by using a Perkin-Elmer 257 spectrophotometer with grating optics.

Reactions of $LiCu(CH_3)_2$ with $LiAlH_4$. To clear ether solutions of $LiCu(CH_3)_2$ (10 mm), prepared by the reaction of methyl lithium with copper (I) iodide in 500 to 700 ml of Et_2O,[6] were added 10, 20, or 60 mm of $LiAlH_4$ at -78° and the reaction mixtures were stirred magnetically under nitrogen until they reached room temperature. These solutions were then filtered in a nitrogen atmosphere under vacuum in order to separate the bright yellow solid which precipitated in every case. The precipitates from each reaction were washed on the filter with 400 to 500 ml of ether. Throughout the filtration and washing procedures, care was taken that a thin film of liquid always covered the solid since it darkened rapidly even on exposure to purified nitrogen. The solid was transferred and stored as a slurry in the final 50 ml portion of wash ether.

(6) H. Gilman, R. G. Jones, and L. A. Woods, J. Org. Chem., 33, 949 (1968).

Samples for analysis were consistently obtained by removing the ether under vacuum from a portion of the slurry and drying the residual bright yellow solid at 10^{-6} mm Hg for 2 hours at room temperature.

Analyses. Products obtained were readily hydrolyzed by water or dilute acids and residual solids that remained after hydrolysis dissolved on addition of concentrated nitric acid. Gas evolution analyses were performed by hydrolyzing tared samples on a standard

vacuum line employing a Toepler pump to collect and measure noncondensable gases. Hydrogen-methane mixtures were identified by gas chromatography and ratios of hydrogen to methane were determined by tensimetric techniques or by measurement of pressure change to weight loss ratios observed during vacuum thermogravimetric analyses using a modified Mettler Thermoanalyzer II. Copper was determined by electrogravimetric analysis and lithium by flame photometric measurement on hydrolysis solutions.

Products were analyzed for possible impurities of aluminum and iodine. Aluminum analyses were carried out by EDTA titration of hydrolysis solutions after copper was removed electrolytically. Volhard titrations were used to determine iodine. However, the only impurity of this nature found in the products was aluminum in the reaction where $LiAlH_4$ was present in 6 fold excess.

Results and Discussion

When ether solutions of $LiCu(CH_3)_2$ and $LiAlH_4$ were combined at -78° and allowed to warm to room temperature, an extremely air sensitive bright yellow solid separated from the clear supernatant liquid. The yellow solid typically contained more than 95% of the copper initially present in solution, and when these reagents were combined in 1:1 ratio, infrared analysis of the supernatant solution indicated that $LiAlH_2(CH_3)_2$ is the predominant aluminum species present after reaction.

These results suggested that reaction (1) occurred as expected to produce insoluble $LiCuH_2$, however, the yellow precipitate proved to

be complex and unstable. When dried and stored in vacuum or nitrogen atmosphere, the solid displayed marked decomposition within 2 to 3 hours. Stored as a slurry in diethyl ether, similar decomposition was in evidence after 24 to 48 hours.

Analyses showed that individual samples of the solid contained variable molar ratios of lithium to copper and that the gases released on hydrolysis were mixtures of hydrogen and methane. The quantity of methane found in various analytical samples ranged from 13 to 20 mole %. An averaged analysis of products showed the following molar ratios of Li:Cu:H:CH_4 respectively: 1.0:1.0:1.7:0.3.

Attempts to force reaction (1) to completion by the use of excess $LiAlH_4$ [$LiCu(CH_3)_3$:$LiAlH_4$, 1:2 and 1:6] did not significantly reduce the quantity of methane found in the hydrolysis gases and led to the inclusion of aluminum impurities in the product.

The possibilities that the methane arose from impurities of CH_3Li or CH_3Cu were examined. CH_3Li is soluble in diethyl ether and reported to react with $LiAlH_4$; the conditions used in these reactions seemed sufficient to eliminate it as a possible impurity. Since nothing appeared to be known about the stability of methyl copper in the presence of $LiAlH_4$, we investigated this possibility under conditions consistent with this investigation. CH_3Cu was found to react with $LiAlH_4$ to produce a black solid which was insoluble in diethyl ether and slowly evolved gases at room temperature. Presumably, the black material was a mixture of metallic copper and unstable copper hydride. A dried sample of this solid evolved on hydrolysis both hydrogen and a small quantity of methane. Substantial aluminum

impurities found in the solid prevented assignment of the origin of methane since species of the type $LiAlH_{4-n}(CH_3)_n$ could have been sufficient to account for both the hydrogen and methane. Therefore, we could not rigorously exclude methyl copper as an impurity in our original reaction but is observed reactivity towards $LiAlH_4$ certainly lessens such a possibility.

Vacuum thermogravimetric analyses suggested that the yellow solid was a mixture of $LiCuH_2$ and $LiCuH(CH_3)$ (Figure 1). The thermogram of a tared sample showed four weight losses accompanied by the release of noncondensable gases assignable to the processes A through D.

(A) Decomposition of $LiCuH(CH_3)$ (60°) with production of methane, methyl lithium, and metallic copper.

(B) Decomposition of $LiCuH_2$ (76°) with production of hydrogen, lithium hydride, and metallic copper.

(C) Decomposition of methyl lithium formed in process A (260°) with production of methane and metallic lithium.

(D) Decomposition of LiH formed in process B (450°) with production of hydrogen and metallic lithium.

These assignments are still tentative since our total data on this system is still insufficient for us to make an unequivocal evaluation of the product produced on reaction of $LiCu(CH_3)_2$ with $LiAlH_4$. Further investigation of this and other reactions designed to prepare Li_2CuH_3 and Li_3CuH_4 should provide pertinent information on the possibility of preparing useful complex hydrides of copper.

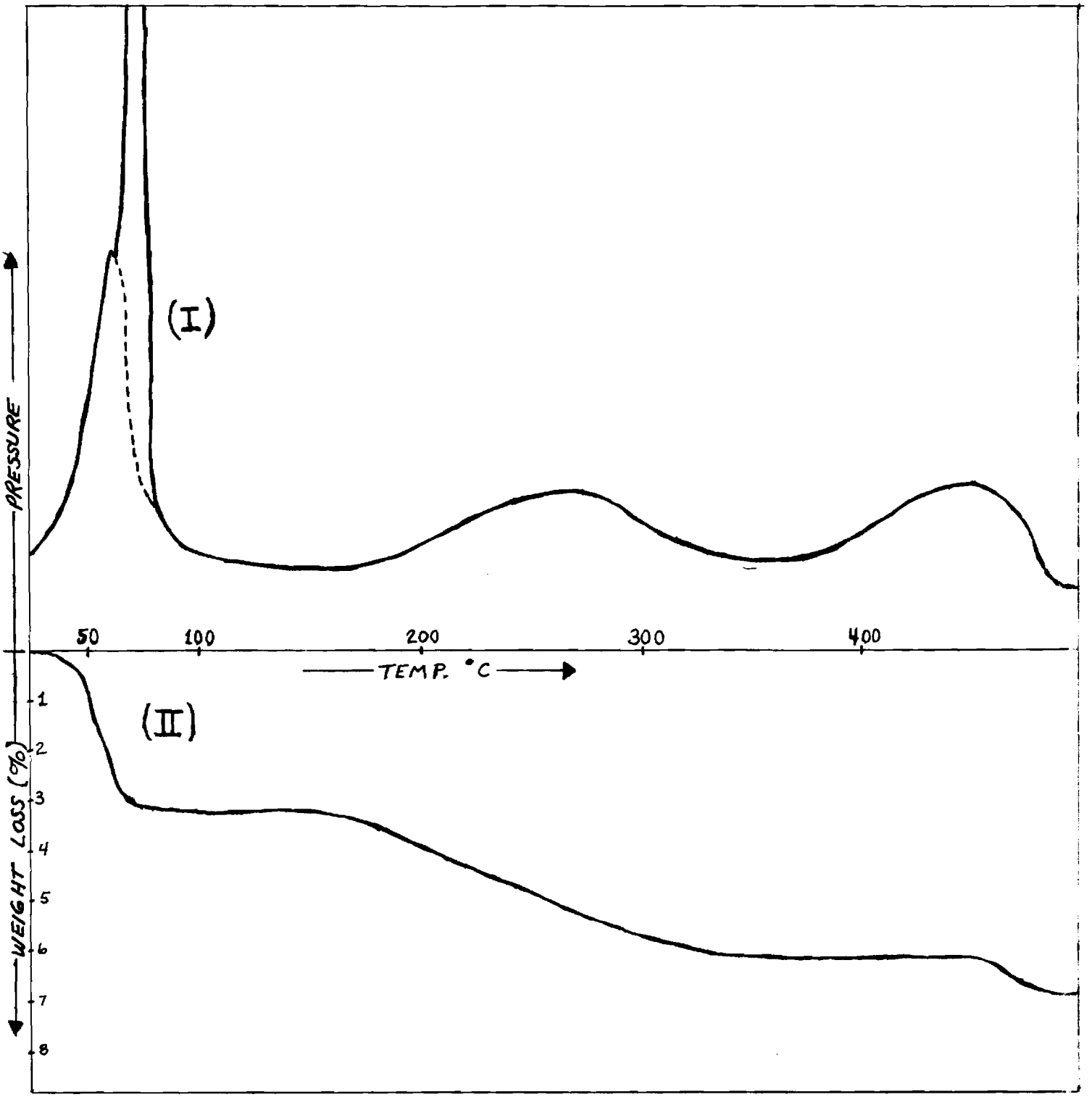


Figure 1. Vacuum thermogravimetric analysis of mixture believed to contain $LiCuH_2$ and LiCuHMe. Curve (II) shows percent weight loss of original sample and Curve (I) displays simultaneous pressure changes associated with loss on noncondensable gases.

Development of High Vacuum DTA-TGA Instrumentation To Be Used For Structure Determination of Complex Metal Hydrides

Pierre Claudy and E. C. Ashby

Abstract

High vacuum DTA-TGA instrumentation has been constructed for structure elucidation of complex metal hydrides. The instrumentation is functioning very well and preliminary results indicate that this instrumentation will play a major role in determining structure-stability relationships.

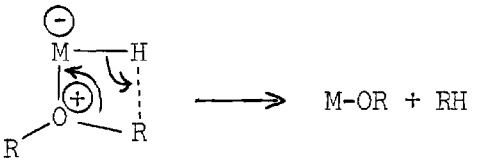
Introduction

Thermal Gravimetric Analysis (TGA) allows one to follow the change of the mass of a compound with temperature. Differential Thermal Analysis makes the comparison between the temperature of the product and that of an inert product and gives the sign of the enthalpy change occurring during a physical reaction (structure change, melting) or chemical change (decomposition, solid gas or solid-solid reaction). These two techniques are complementary and very often can be utilized simultaneously on the same instrumentation.

In practice, there are a number of problems involved in using DTA-TGA especially with very air sensitive compounds like hydrides. If the experiments are carried out under gas flow, apparent changes of weight and thus poor reproduction are seen. This arises from the change in gas density with temperature (below 500°), convection currents, or changes of the flow rate however small. It is very difficult, if

not impossible, to avoid a slight oxidation of the product by the small quantities of water or oxygen either introduced by the carrier gas or that which remains after degassing of the TGA. In addition, the mass change due to hydrogen loss is small and thus, the precision of the experiment is not as great as desired.

Many hydrides contain variable amounts of ether. Unfortunately, this presents a problem in that the ether can react with the hydride.



In order to avoid ether cleavage problems to a large extent, the DTA-TGA experiments must be carried out under vacuum (10^{-2} - 10^{-3} T). The following additional problems are lessened or completely avoided.

(1) Weight change with temperature (below 500°)

(2) Oxidation

(3) Ether will be removed at lower temperatures, thus lessening ether cleavage.

It should be very useful to have a quantitative analysis of the gas evolved at the conclusion of the experiment and to have an analysis, at least qualitative, during the TGA.

Principle of the Apparatus. A Mettler Thermoanalyzer II and Welch Pump were used to construct the modified DTA-TGA instrumentation. The dynamic pressure in the vacuum line depends only on the amount of gas evolved since the flow rate of the pump is fixed by construction. If we know the mass loss of the compound, it is qualitatively possible

to know the nature of the gas. For example, if ten milligrams of ether or hydrogen are lost, the volumes of gas are greatly different and hence, the pressure peaks during the evolution. However, for a mixing of two (or more) gases it is more difficult to get this information. But an easy separation is possible if one of the two gases is trapped in liquid nitrogen. Under these conditions, the pressure before the cold trap will be higher than after the cold trap, and thus a precise determination is possible.

The condensed gas can be qualitatively analyzed. The principle of this analysis has been previously described. Under vacuum the trap is slowly warmed and the solids sublimed (under the experimental conditions the compounds are below the triple point) when the temperature of the trap is greater than the solid sublimation temperature under the experimental conditions. The vapor pressure is recorded by use of a vacuum gauge. By standardization it is possible to construct a curve which relates the area of the peak versus the quantity of product. The warming is reproducible and thus the measure of zero time and the appearance of a compound is characteristic of the compound. For hydrides, ethers and any carbon compounds with 3 atoms or more are trapped in liquid nitrogen.

Realization (see Figure 1).

(1) Gauges. The most difficult problem is to have vacuum gauges whose tension-pressure response is the same. In this view chromatographic filaments "GOW Mac Instrument" have been used. They are supplied with a constant current (21.3 ma) and the tension which appears depends on the pressure (Figure 2) and on the thermal conduct-

ivity of the gas. The hydrogen peak will be spread out and that is advantageous. Empirically, an adjustment has been made to get the same pressure on both gauges with an incondensable gas (Ar)

(2) Description of the Vacuum Line. The vacuum line has been constructed to allow the use of the TGA under various conditions: vacuum, static pressure, or gas flow. In this case the gas enters the TGA by V and leaves through r_1 or r_2 and r_3; R_2 open, R_1 closed.

Between R_1 and the pump is the analytical device: it is a simple U-shape tube (diameter 16 mm). One branch has a copper part, the shape of which must obey the following:

-- slow warming after removing the liquid nitrogen because the quantity of product to analyze can be great (more than 2 mg).

-- vertical thermal gradient to assure a good separation of the trapped products.

On the top of the trap is the analysis gauge J_1. The second trap is as near as possible to the exit of the analysis device. The efficiency must be very good because the gas transfer during the analysis is mostly made by cool pumping.

Results

Test. The complete apparatus must be tested with a compound which evolves different gases, both condensable and non-condensable, at different intervals. Calcium oxalate, $CaC_2O_4 \cdot H_2O$, was chosen, the TGA was carried out with the same heating rate: 2°C/mn, and the product was placed in a platinum crucible.

The thermal decomposition occurs in 3 different steps:

$$CaC_2O_4 \cdot H_2O \xrightarrow{R.T.\ 110} CaC_2O_4 + H_2O \quad (1)$$

$$CaC_2O_4 \xrightarrow{400} CaCO_3 + CO \quad (2)$$

$$CaCO_3 \xrightarrow{500\text{-}650} CaO + CO_2 \quad (3)$$

In Figure 3 are shown:

-- the TGA $\frac{\Delta P}{P}$ %

-- the DTG $\frac{\Delta P}{\Delta C}$ mg/c calculated from the TGA

-- the pressure curves of both gauges J_1 and J_2

For reactions (1) and (3) J_2 records a pressure but J_1 stays to the limit of the vacuum. On the contrary during the reaction (2) J_1 and J_2 give a similar pressure. The results are consistent with what is expected; H_2O and CO_2 are condensed and CO is not.

The DTG gives the same indication as the pressure curves, only the amplitudes of the peaks are different. The maximum of the DTG and pressure curve have a small difference with temperature, which comes from the damping of the TG apparatus and the disturbance of the weight due to the gas evolution. There is no weight shift with the temperature.

To make an evaluation of the detection of non-condensable gas in the condensable gas, TGA analysis with different quantities of product has been carried out and the curve $S = f(m_{CO})$ obtained with J_1 (Figure 4) should give CO in CO_2 in an exact stoichiometry according the the equation:

$$ZnC_2O_4 \longrightarrow ZnO + CO + CO_2$$

where CO and CO_2 are evolved together.

Thermal Decomposition of $Mg(AlH_4)_2$. For hydrides a special crucible is used (Figure 1). The experiment has shown that when H_2 is evolved, very often product particles are thrown out of the crucible. To avoid this, the crucible is closed by a fritted glass disk through which gas can escape but no solid. The temperature is, therefore, limited to 500°, which is sufficient for any hydride.

The TGA of $Mg(AlH_4)_2 \cdot 0.595$ THF is shown in Figure 5. The THF is evolved in two stages between 40 and 140° which suggests that THF can be bonded in two different ways. During this evolution a small reaction between THF and the hydride is noticed because a small amount of non-condensable gas is recorded. A possible explanation is represented below.

$$Mg(AlH_4)_2 \cdot x\ THF \longrightarrow Mg(AlH_4)_2 + x\ THF$$

then the decomposition starts according to:

$$Mg(AlH_4)_2 \xrightarrow{150°} MgH_2 + 2\ Al + 3/2\ H_2$$

It was interesting to study in more detail the latter reaction, because it is known that with alkali metal aluminum hydrides there is in fact a two stage decomposition.

$$3\ M\ AlH_4 \longrightarrow M_3AlH_6 + 2\ Al + 3\ H_2$$

$$M_3AlH_6 \longrightarrow 3\ MH + Al + 3/2\ H_2$$

Isothermal decomposition was also carried out. At 110° THF was rapidly evolved (2 hours) without any decomposition. A white product is obtained; the X-ray analysis is reported (Table I, 1). At T = 115° the decomposition is slow, and when the hydrogen evolution was half the expected, the TGA was stopped and the gray residue containing the same white crystals was examined (Table I, 2). Finally, the pyrolysis was carried out at 200° and the X-ray diagram showed only MgH_2 and Al (Table I, 3).

The identity of 1 and 2 where only the X-ray lines of Al are visible, gives the proof that the same compound is present, namely, $Mg(AlH_4)_2$. Therefore, the thermal decomposition is:

$$Mg(AlH_4)_2 \longrightarrow MgH_2 + 2\,Al + 3\,H_2$$

However, the expected MgH_2 spectra is not obtained in Table I, 2 and it is believed that its intensity is too weak to be observed.

Analysis. A record made at the end of an experiment with $Mg(AlH_4)_2 \cdot 2THF$ is represented in Figure 6. Three initial small peaks could not be identified. Then the peak for THF appeared and one for H_2O which is followed by two other peaks. The first one is C_4H_9OH coming from the THF hydrogenolysis.

The various experiments with different quantities of $Mg(AlH_4)_2 \cdot xTHF$ gave the standardization curve $S = f(m_{THF})$, see Figure 7. From the experimental data in the 5-15 mg range the precision is $\pm$ 3%.

m_{THF}	6.95	9.3	9.5	10.6	13.2	14.4	14.4	26.5
S	75	222	214	239	295	298	304	446

If a better curve is needed, particularly for small quantities, it is easy to use the volume v between r_1 and r_2. A known pressure of THF is introduced and sent into the trap. Known v, P, T, gives the mass of the THF and then the desired curve.

The separation power is not very good because large samples can be admitted and as a result of the principle of the analysis, a weak resolution is obtained.

Conclusion

The modified apparatus enables us to make a qualitative analysis of gas evolved during a TGA-DTA of a hydride. At the end of an experiment a quantitative analysis of the condensed gas can be made with an accuracy of 3%. It is possible, on stopping the TGA at various steps of the decomposition and making the gas analysis, to know the nature and the amount of condensable gases evolved.

Table I. X-Ray Diffraction Data

(1)	(2)	(3)	Al	MgH_2
5.55				
5.6	5.5			
4.75	4.8			
4.1				
3.95	3.90			
3.50	3.50			
3.20	3.30			
3.10	3.15	3.14		3.19
2.85	2.82			
2.75				
2.56	2.51	2.57		2.51
		3.49		
2.42	2.42			
	2.31	2.32	2.33	
		2.22		2.26
	2.07			
9.00	2.00	2.00	2.024	
1.98				
1.92	1.93			
1.77	1.77			
1.62	1.62	1.66		1.679
1.55	1.55	1.58		1.595
1.48	1.48			
1.455	1.46			
	1.42	1.42	1.431	1.427
		1.36		1.364
		1.34		1.347
1.29	1.29			
		1.24	1.221	1.255
		1.215		

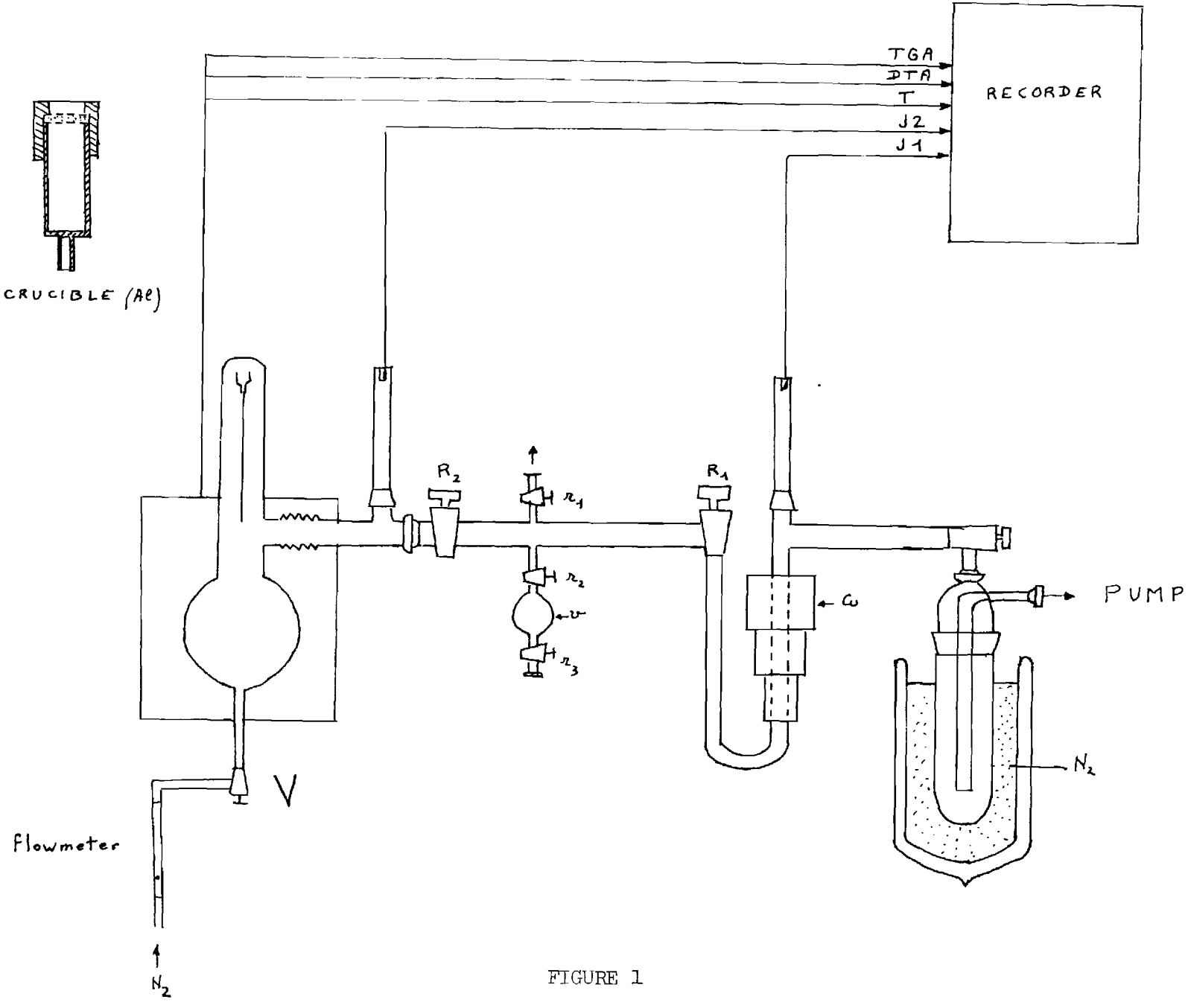

TGA
DTA
T
J2
J1
RECORDER
CRUCIBLE (Al)
R2
R1
π1
π2
π3
V
ω
PUMP
N2
Flowmeter
V
N2

FIGURE 1

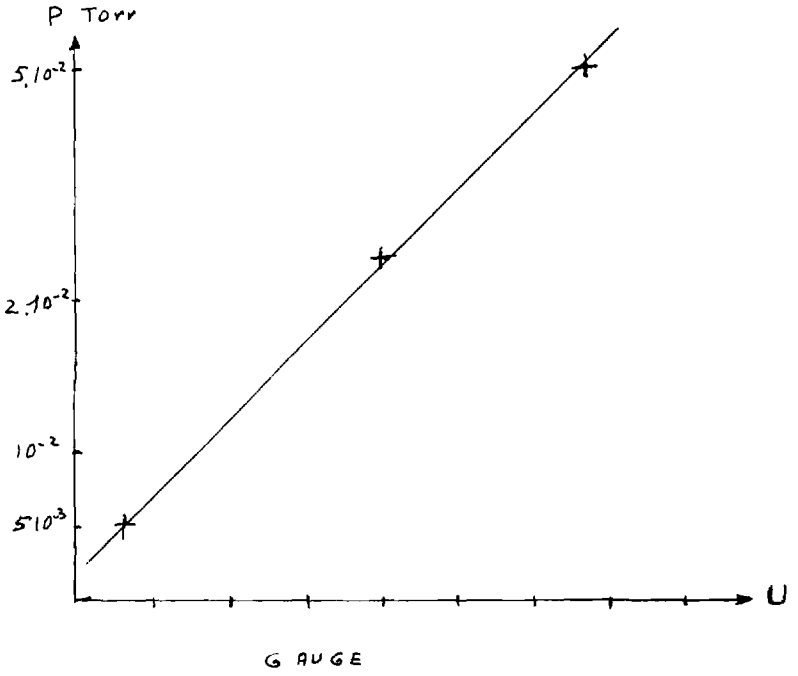


FIGURE 2

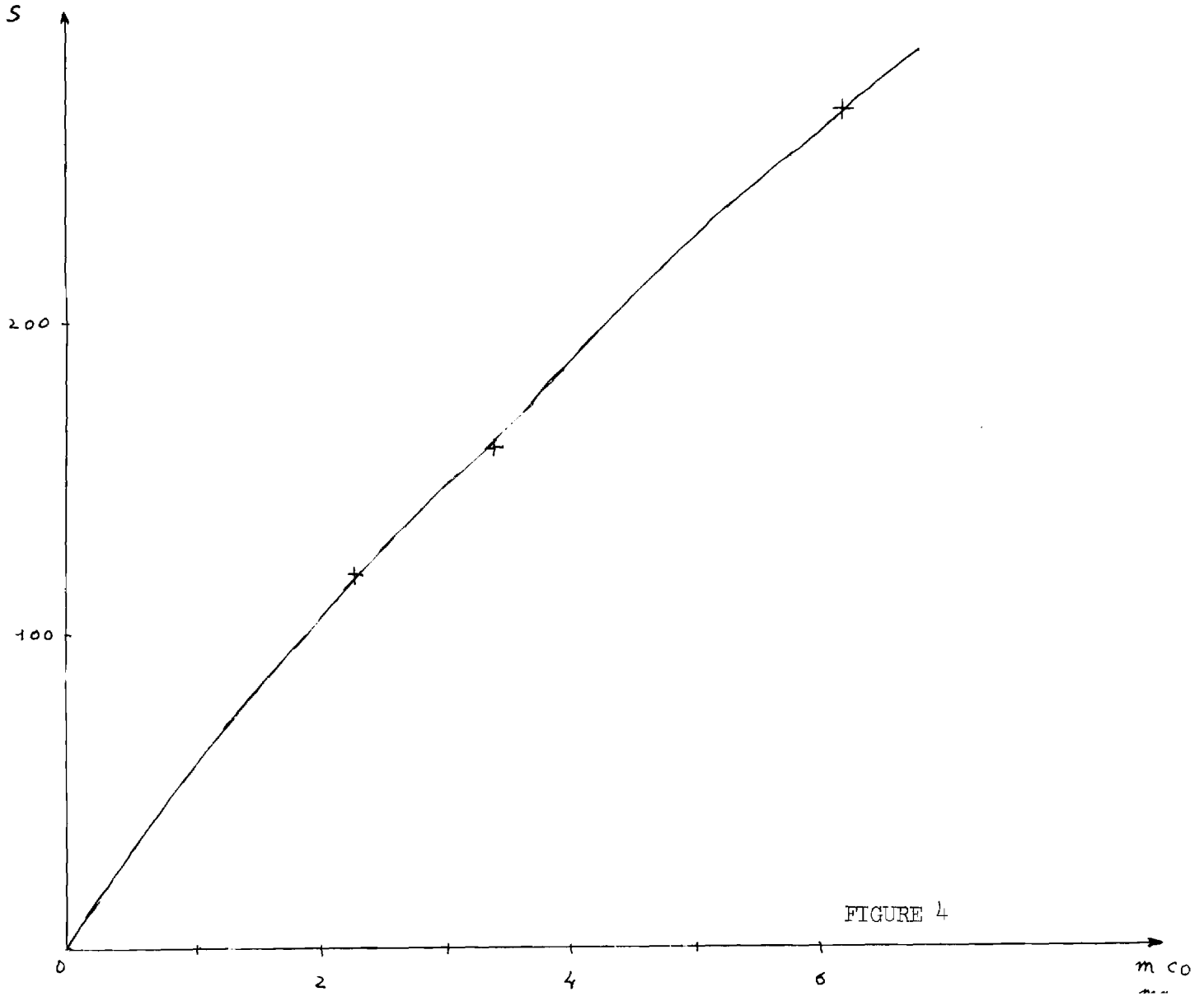


FIGURE 4

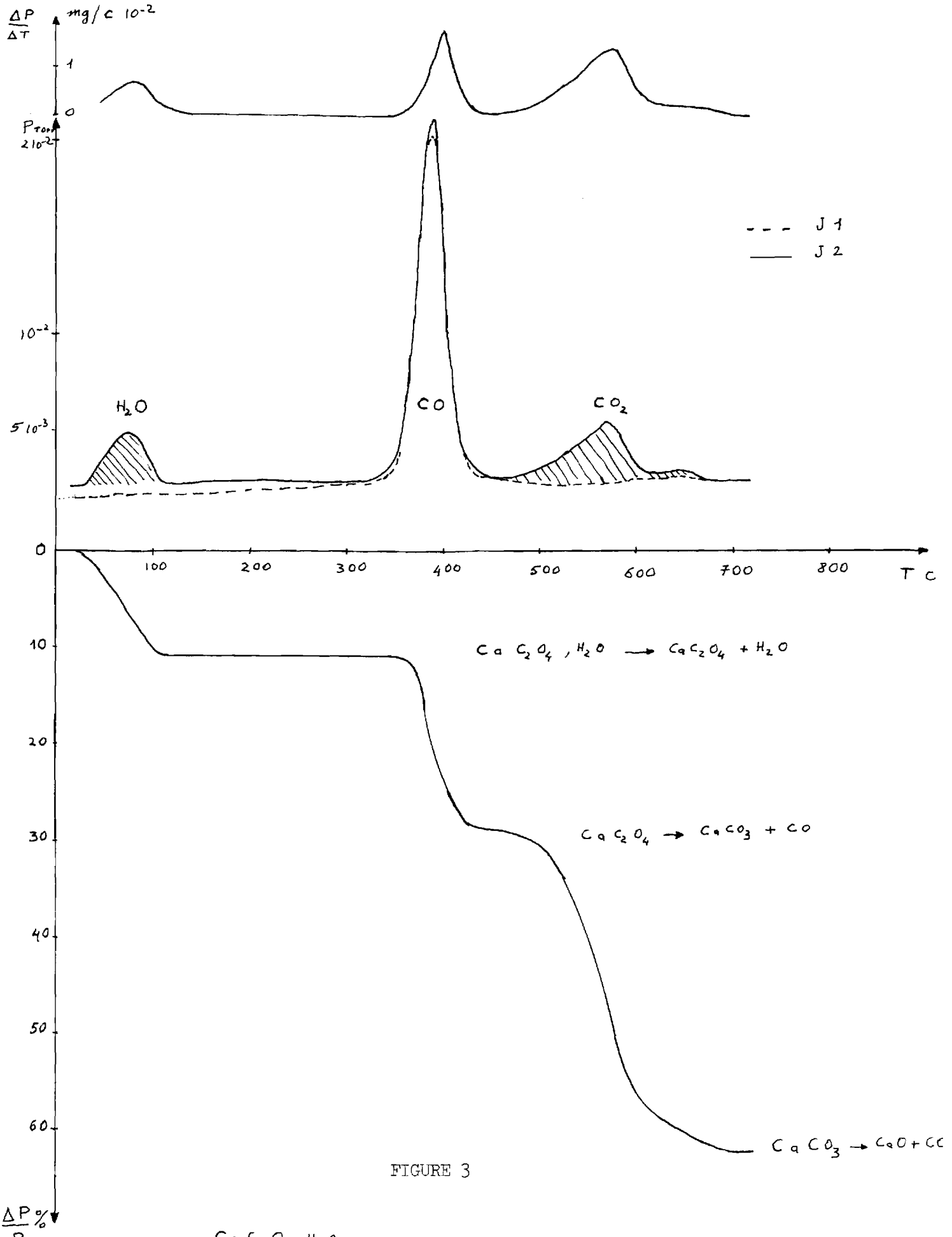


FIGURE 3

$Ca\,C_2O_4\,,H_2O$ 34,8 mg 2 c/mn.

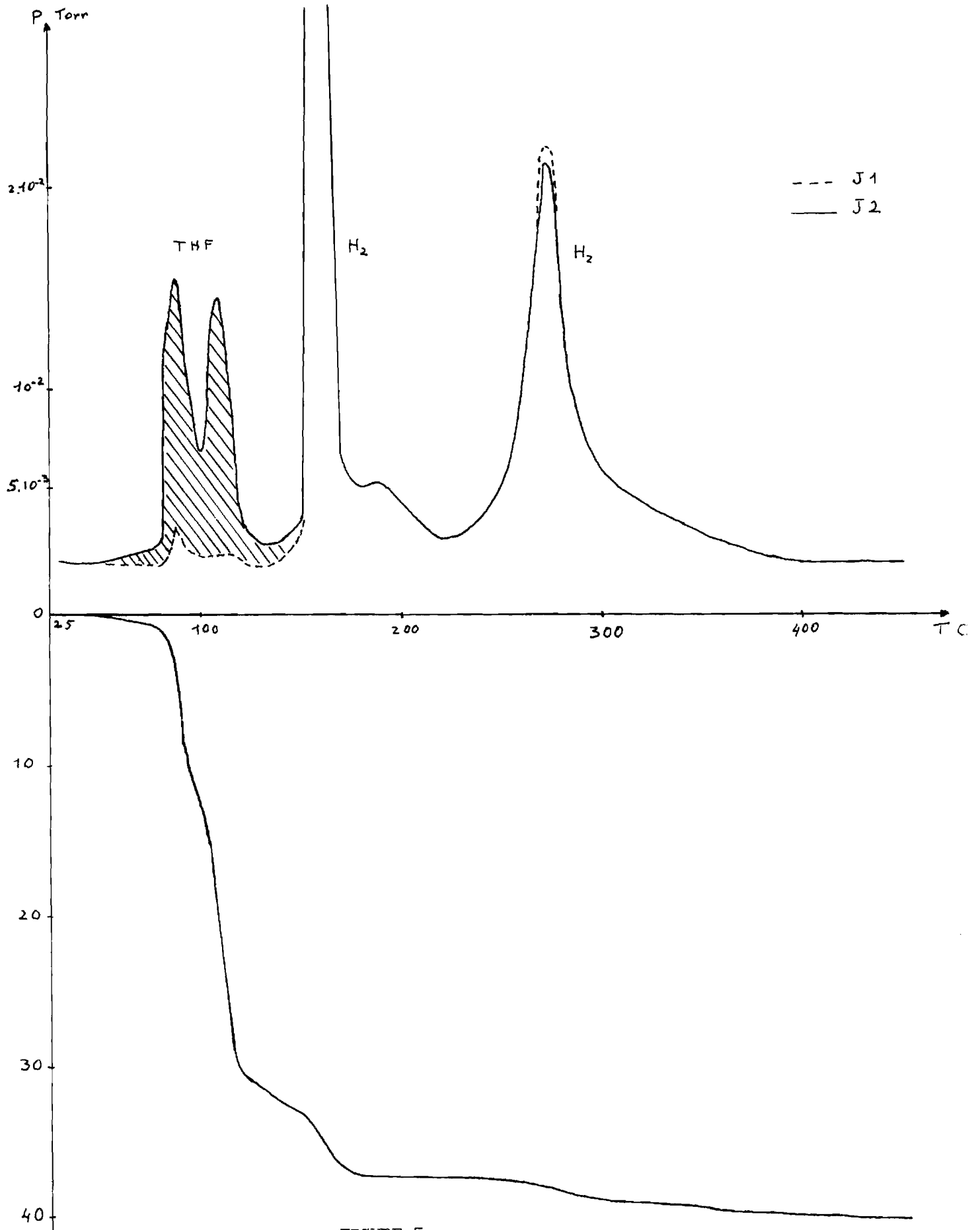


FIGURE 5

$Mg(AlH_4)_2$ x THF

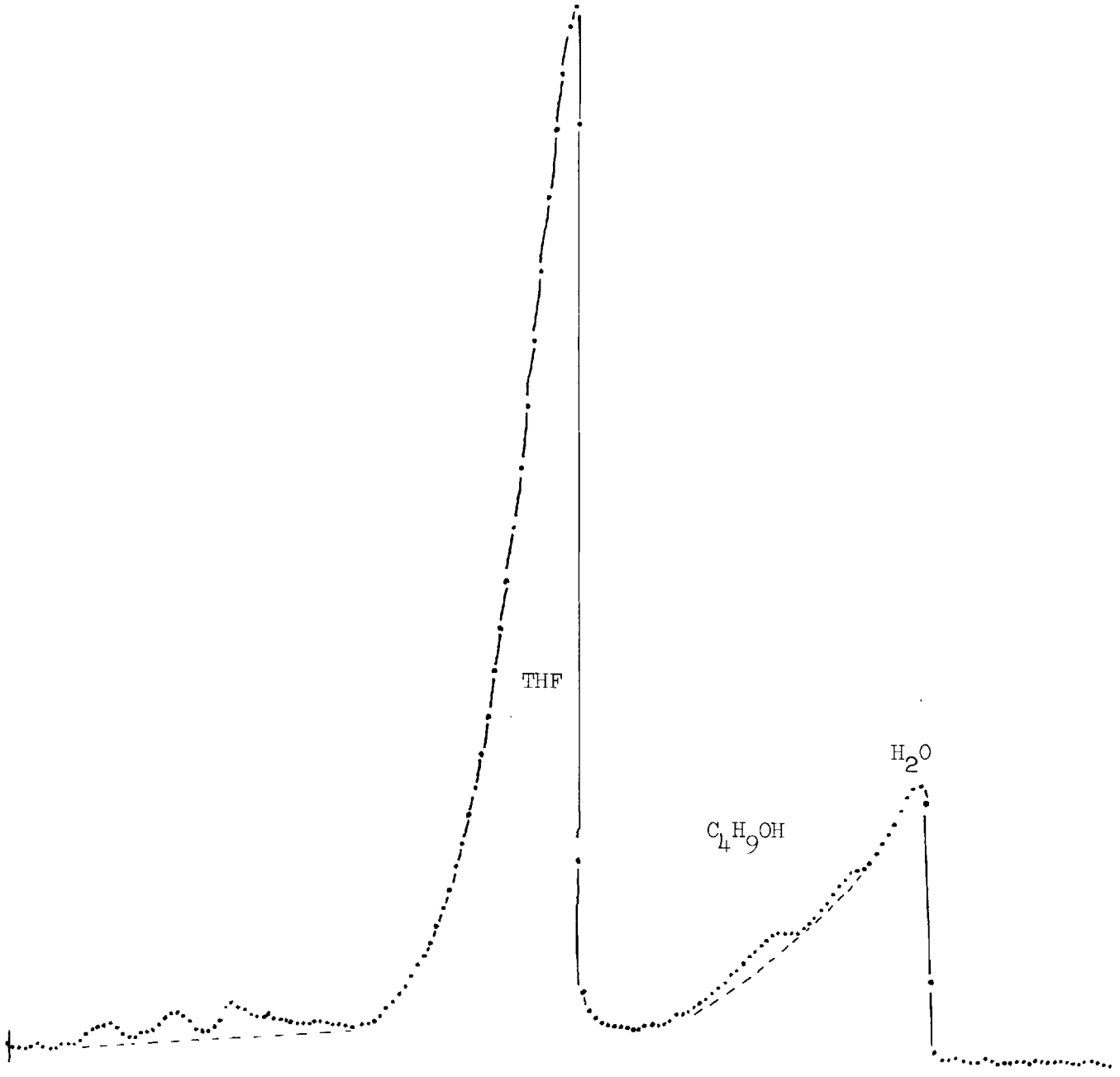


FIGURE 6

Concerning the Existence of $HMgAlH_4$ and $HMgBH_4$

E. C. Ashby and R. D. Schwartz

Abstract

Seven methods for the preparation of $HMgAlH_4$ and $HMgBH_4$ have been investigated.

$$MH + XMgAlH_4 \rightarrow MX + HMgAlH_4$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + Olefin$$

$$RMgAlH_4 \xrightarrow[H_2]{\Delta} RH + HMgAlH_4$$

$$RMgAlH_4 + MH \rightarrow MR + HMgAlH_4$$

$$Mg(AlH_4)_2 + L \rightarrow HMgAlH_4 + AlH_3 \cdot L$$

$$MgH_2 + AlH_3 \rightarrow HMgAlH_4$$

$$MgH_2 + Mg(AlH_4)_2 \rightarrow 2\ HMgAlH_4$$

In all of these reactions a mixture of MgH_2 and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ were isolated rather than the expected $HMgAlH_4$ or $HMgBH_4$. The conclusion from this work is that $HMgAlH_4$ and $HMgBH_4$ disproportionate to MgH_2 and $MgAlH_4$ or $MgBH_4$. Borane and alane extraction of complex magnesium borohydrides and aluminohydrides with sodium and lithium hydride have been shown to be general reactions. Other important observations concerning fundamental transformations in hydride chemistry are reported.

Introduction

The preparation of compounds of the type $HMgBH_4$ and $HMgAlH_4$ have been investigated previously. In 1940 Burg and Schlesinger[1] reported

(1) A. B. Burg and H. I. Schlesinger, J. Amer. Chem. Soc., 62, 3425 (1940).

the preparation of $HBeBH_4 \cdot N(CH_3)_3$ by borane extraction of $Be(BH_4)_2$ with trimethylamine.

$$Be(BH_4)_2 + 2[N(CH_3)_3] \rightarrow HBeBH_4 \cdot N(CH_3)_3 + BH_3N(CH_3)_3 \qquad (1)$$

In 1951 Schlesinger[2] and coworkers reported that the addition

(2) G. B. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilbach, and H. I. Schlesinger, J. Amer. Chem. Soc., 73, 4585 (1951).

of diethylmagnesium to a large excess of lithium aluminum hydride in diethyl ether followed by addition of benzene resulted in the precipitation of a solid with the empirical formula $HMgAlH_4$. Unfortunately, the compound was not characterized further.

$$LiAlH_4 + Mg(C_2H_5)_2 \rightarrow HMgAlH_4 + \text{Other Products} \qquad (2)$$

A recent investigation of the reaction of the above reaction[3] has shown

(3) E. C. Ashby and R. G. Beach, Inorg. Chem., 9, 2300 (1970).

that $HMgAlH_4$ is not produced in this reaction.

In this paper we would like to report our attempts to prepare and characterize $HMgAlH_4$ and $HMgBH_4$.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[4] or at the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

(4) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

Instrumentation. - Infrared spectra were obtained in cesium iodide cells using a Perkin Elmer Model 621 High Resolution Infrared Spectrophotometer. X-ray powder diffraction patterns were obtained using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately prior to use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from the Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride, sodium hydride (57% suspension in mineral oil) and sodium borohydride were obtained from Ventron Metal Hydrides Division.

Magnesium aluminum hydride, chloromagnesium aluminum hydride, iodomagnesium aluminum hydride and magnesium halide were prepared as described previously.[5]

(5) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

Analytical Procedures. - Halogen analysis was carried out by the Volhard Method. Aluminum and magnesium analyses were carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen was analyzed by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated bulb via a Topler pump after passing the gas through a liquid nitrogen trap.

Preparation of Lithium Hydride. - Lithium hydride was prepared as described previously.[6] The solid, obtained as a slurry in pentane,

(6) E. C. Ashby and R. D. Schwartz, Inorg. Chem., 10, 355 (1971).

gave a lithium to hydrogen ratio of 1.00:1.00.

Preparation of $(n\text{-}C_4H_9)_3SnH$. - Tri-n-butyltin hydride was prepared as described previously.[7] The compound was distilled at 70°/6 mm. The

(7) W. P. Neumann, Angew. Chem. Internat. Ed., 2, 165 (1963).

infrared spectrum of the neat compound showed an absorption at 1810 cm^{-1} characteristic of tri-n-butyltin hydride.

Preparation of $ClMgBH_4$. - Chloromagnesium borohydride was prepared as described previously.[8] Analysis of the product in solution showed a Mg:Cl ratio of 1.00:1.04. The infrared spectrum in tetrahydrofuran showed B-H absorptions at 2380 and 2175 cm^{-1}.

(8) W. E. Becker and E. C. Ashby, Inorg. Chem., 4, 1816 (1965).

Preparation of $C_2H_5MgBH_4$ and s-$C_4H_9MgBH_4$. - Ethyl magnesium borohydride was prepared as described previously.[5] s-Butylmagnesium borohydride was prepared in a similar fashion. Analysis of the latter product in solution showed a Mg:Cl ratio of 1.0:0.02. The infrared spectrum of the solution showed bands at 2420, 2220, and 535 cm^{-1}.

Preparation of $HMgAlH_3(C_2H_5)$ and $HMgAlH_3$(n-C_4H_9). - These compounds were prepared exactly as described previously.[9]

(9) E. C. Ashby and R. D. Schwartz, Inorg. Chem., (in press).

Attempts to Prepare $HMgAlH_4$ and $HMgBH_4$. - As indicated by the "Results and Discussion" section, numerous attempts were made to prepare $HMgAlH_4$ and $HMgBH_4$ by a variety of methods. Only a few examples are provided here in order to represent the type of experimental approach taken to evaluate the methods.

Reaction of Sodium Hydride and $ClMgAlH_4$ in Tetrahydrofuran. - To 50 ml of chloromagnesium aluminum hydride in THF (0.2056 M) was added 454.5 mg sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days. The solution was then filtered and the filtrate

gave on analysis of Cl:Mg:Al ratio of 0.0:1.0:1.88. From the filtration was isolated 1.96 gm of solid. The infrared spectrum of the solid gave bands at 1725, 1025, 975, 790, and 745 cm^{-1}. The X-ray powder pattern of the solid gave lines corresponding to sodium chloride, magnesium aluminum hydride and magnesium hydride.

Reaction of Sodium Hydride and $ClMgBH_4$ in Tetrahydrofuran. - To 45 ml of chloromagnesium borohydride in THF (0.4887 M) was added 1.925 gm of sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days and then filtered. The infrared spectrum of the filtrate showed no bands other than those assigned to THF. The X-ray powder pattern of the solid resulting from the filtration gave lines corresponding to sodium chloride, sodium borohydride and magnesium hydride. The infrared spectrum of the solid gave bands corresponding to sodium borohydride and magnesium hydride.

Reaction of $ClMgAlH_4$ and Sodium Hydride in Tetrahydrofuran in the Presence of N,N,N',N'-Tetramethylethylene Diamine. - To 75 ml of chloromagnesium aluminum hydride in tetrahydrofuran (0.2345 M) was added 11 ml of TMED and 739.6 mg sodium hydride (57% in mineral oil). The solution was stirred for two days and then filtered. The analysis of the filtrate gave a Mg:Al:Cl ratio of 0.81:1.1:0.5. This represented about 70% reaction. The infrared spectrum of the solution after filtration had a band at 1715 cm^{-1} corresponding to the Al-H stretching band in chloromagnesium aluminum hydride. The solid obtained from filtration exhibited bands at 1725, 1665, 1025, 1010, 940 (B), 870, 790, 760, and 590 cm^{-1}. The X-ray powder pattern of the solid showed lines corresponding to sodium chloride, magnesium

aluminum hydride and magnesium hydride.

Reaction of $Mg(AlH_4)_2$ with $N(CH_3)_3$. - Magnesium aluminum hydride (3.29 mmoles) was added to 20 ml of benzene in a sealed tube reactor. Twenty mmoles of trimethylamine was added at -196°. The mixture was then sealed under vacuum and the mixture was allowed to stand at room temperature for 10 days. The resulting mixture was filtered and the analysis of the solid from filtration gave Mg:H ratio of 1.0:1.98. The infrared spectrum and X-ray powder pattern of the solid corresponded to MgH_2. The analysis of the filtrate showed it to contain no magnesium but 95 percent of the original aluminum. The infrared spectrum of the filtrate was characteristic of $AlH_3 \cdot 2N(CH_3)_3$.

Results and Discussion

The reactions employed in the attempts to prepare $HMgAlH_4$ and $HMgBH_4$ can be divided into seven general categories (eq. 3-9). The first reaction (eq. 3) involves the reduction of a compound of empirical formula $XMgAlH_4$ or $XMgBH_4$ by a chemical source of hydride ion, e.g., NaH.

$$Mg + XMgAlH_4 \rightarrow MX + HMgAlH_4 \quad (3)$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + \text{Olefin} \quad (4)$$

$$RMgAlH_4 \xrightarrow[H_2]{\Delta} RH + HMgAlH_4 \quad (5)$$

$$RMgAlH_4 + MH \rightarrow MR + HMgAlH_4 \quad (6)$$

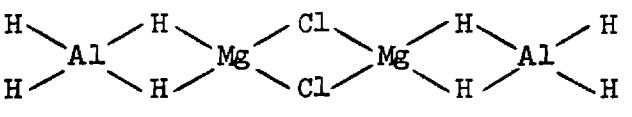
$$Mg(AlH_4)_2 + L \rightarrow HMgAlH_4 + AlH_3 \cdot L \quad (7)$$

$$MgH_2 + AlH_3 \rightarrow HMgAlH_4 \quad (8)$$

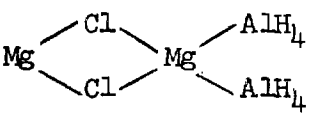
$$MgH_2 + Mg(AlH_4)_2 \rightarrow 2\ HMgAlH_4 \quad (9)$$

The second method (eq. 4) involves the pyrolysis of a compound of empirical formula $RMgAlH_4$ or $RMgBH_4$. The third method (eq. 5) involves the high pressure hydrogenolysis of $RMgAlH_4$ or $RMgBH_4$ compounds. The fourth method (eq. 6) involves the metathetical exchange between a metal hydrogen compound and $RMgAlH_4$ or $RMgBH_4$. The fifth method (eq. 7) involves extraction of aluminum hydride from $Mg(AlH_4)_2$. The sixth method (eq. 8) involves the direct addition of aluminum hydride to MgH_2. The final method (eq. 9) involves the redistribution of MgH_2 and $Mg(AlH_4)_2$.

MH + $XMgAlH_4$. - In an attempt to prepare $HMgAlH_4$ according to eq. 3, sodium hydride was allowed to react with chloromagnesium aluminum hydride in THF at a molar ratio of 1:1. After several days the solution was filtered. Over 90% of the reaction product was insoluble in the solvent. Elemental analysis of the filtrate gave a Cl:Mg:Al ratio of 0.0:1.0:1.88. The filtrate consisted of a dilute solution of $Mg(AlH_4)_2$ as determined by infrared analysis. The solid isolated by filtration had an infrared spectrum exhibiting bands at 1725, 1025, 975, 790, and 745 cm^{-1} characteristic of $Mg(AlH_4)_2 \cdot 4$ THF. The X-ray powder pattern of the solid confirmed that it was a physical mixture of sodium chloride, magnesium hydride, and magnesium aluminum hydride. The conclusion to be drawn from this experiment depends on the structure of the reactant (dimer $ClMgAlH_4$).



I



II

If $ClMgAlH_4$ has the structure indicated by I then the conclusion is that $HMgAlH_4$ is produced in the above reaction but disproportionates to MgH_2 and $Mg(AlH_4)_2$.

$$NaH + ClMgAlH_4 \rightarrow NaCl + HMgAlH_4 \rightarrow 1/2\ MgH_2 + 1/2\ Mg(AlH_4)_2 \qquad (10)$$

On the other hand, if $ClMgAlH_4$ has structure II then the conclusion is that MgH_2 and $Mg(AlH_4)_2$ are produced in the above reaction without going through an intermediate $HMgAlH_4$.

In an effort to stabilize $HMgAlH_4$ toward disproportionation chloromagnesium aluminum hydride was allowed to react with sodium hydride in the presence of triethylamine and TMED. Since the possibility of AlH_3 extraction exists, weakly basic amines were used. In one experiment $ClMgAlH_4$ was first complexed with the chelating amine TMED, however, some aluminum hydride extraction did occur in addition to the formation of NaCl, $Mg(AlH_4)_2$ and MgH_2.

In another reaction lithium hydride was added in excess as a pentane slurry to iodomagnesium aluminum hydride in diethyl ether. The purpose of this experiment lies in the fact that LiI is soluble in diethyl ether and, hence, if $HMgAlH_4$ is formed, it should precipitate clearly from the reaction mixture. The solution was filtered after several days and the elemental analysis of the filtrate gave a I:Mg:Al ratio of 1.52:0.0:1.0. The infrared spectrum of the filtrate corresponded to lithium aluminum hydride. The solid obtained from the filtration of the reaction mixture gave an infrared spectrum and an X-ray powder pattern characteristic of magnesium hydride. When the lithium hydride was added to iodomagnesium aluminum hydride in a 1:1 ratio, the infrared spectrum of

the solution after stirring for several days corresponded to lithium aluminum hydride. The infrared spectrum and X-ray powder pattern of the solid obtained by filtration of the reaction mixture corresponded to a mixture of lithium iodide, magnesium hydride and unreacted iodomagnesium aluminum hydride. Thus, the reaction seems to proceed by both aluminum hydride extraction (eqs. 11 and 12) and by metathetical exchange followed by disproportionation (eqs. 13 and 14).

Aluminum Hydride Extraction:

$$LiH + IMgAlH_4 \rightarrow LiAlH_4 + IMgH \quad (11)$$

$$2(IMgH) \rightarrow MgH_2 + MgI_2 \quad (12)$$

Metathetical Exchange:

$$LiH + IMgAlH_4 \rightarrow LiI + HMgAlH_4 \quad (13)$$

$$2(HMgAlH_4) \rightarrow MgH_2 + Mg(AlH_4)_2 \quad (14)$$

MH + $XMgBH_4$. - When sodium hydride (in excess) was allowed to react with chloromagnesium borohydride in THF, the resulting solid was shown by X-ray powder pattern analysis to be a mixture of sodium chloride, sodium borohydride and magnesium hydride. This reaction also presumably proceeds via BH_3 extraction in the presence of excess NaH and/or via metathetical exchange as represented by equations 15-20.

Borane Extraction:

$$NaH + ClMgBH_4 \rightarrow NaBH_4 + HMgCl \quad (15)$$

$$2(HMgCl) \rightarrow MgH_2 + MgCl_2 \quad (16)$$

$$MgCl_2 + 2(NaH) \rightarrow MgH_2 + 2\ NaCl^8 \quad (17)$$

(8) E. C. Ashby and R. D. Schwartz, Inorg. Chem., 10, 355 (1971).

Metathetical Exchange:

$$NaH + ClMgBH_4 \rightarrow NaCl + HMgBH_4 \quad (18)$$

$$2(HMgBH_4) \rightarrow MgH_2 + Mg(BH_4)_2 \quad (19)$$

$$Mg(BH_4)_2 + 2\ NaH \rightarrow 2\ NaBH_4 + MgH_2 \quad (20)$$

However, the overall reaction results in the formation of only NaCl, MgH_2 and $NaBH_4$.

Chloromagnesium borohydride is monomeric in THF,[9] however, its

(9) W. E. Becker and E. C. Ashby, Inorg. Chem., 4, 1816 (1965).

composition in solution is not known with certainty. Therefore, the conclusion to be drawn from these results are similar to those of the reaction of NaH and $ClMgAlH_4$. If $ClMgBH_4$ exists in solution as monomeric $MgBH_4$, then we can conclude that the intermediate $HMgBH_4$ disproportionates. However, if $ClMgBH_4$ exists in solution as an equilibrium mixture containing $MgCl_2$ and $Mg(BH_4)_2$, then the normal course of reaction might produce a mixture of MgH_2 and $Mg(BH_4)_2$ without going through the intermediate $HMgBH_4$.

When lithium hydride was stirred with chloromagnesium borohydride, no reaction was detected after several days.

$$LiH + ClMgBH_4 \xrightarrow{THF} \text{no reaction} \quad (21)$$

$HMgAlH_3R$ Pyrolysis. - In the pyrolysis experiments, hydridomagnesium n-butyltrihydridoaluminate [$HMgAlH_3(n\text{-}C_4H_9)$] was suspended in light mineral oil. The slurry was heated under vacuum at 80° for several hours, however

elemental and infrared analysis of the resulting solid product showed it to be recovered starting material. Similar results were obtained in octane solution.

In the compounds represented empirically as $RMgAlH_4$, the alkyl group is actually bonded to aluminum[9] ($HMgAlH_3R$) and is much more stable than if it were bonded to magnesium. With this in mind, higher pyrolysis temperatures were studied. When the solvent was removed under vacuum from an ether solution of $HMgAlH_3(n\text{-}C_4H_9)$, a white solid resulted which was then heated under vacuum. When the temperature reached 150°, drops of liquid began collecting on the upper reaches of the flask and the solid began to turn gray. The sample was then cooled, hexane added and the mixture filtered. The filtrate gave an Al:Mg:H ratio of 1.45:0.0:1.0. The X-ray powder pattern of the resulting solid showed lines corresponding to magnesium hydride, aluminum metal and unreacted $HMgAlH_3(n\text{-}C_4H_9)$. These results indicate that before the alkyl group is removed by pyrolysis, the compound $HMgAlH_3R$ decomposes to MgH_2 and $RAlH_2$. However, $RAlH_2$ compounds are known to disproportionate to the more stable R_2AlH compounds and AlH_3 followed by decomposition of AlH_3 to Al, H_2 and intermediate Al-H compounds at 150°.

$$HMgAlH_3R \xrightarrow{\Delta} MgH_2 + RAlH_2 \qquad (22)$$

$$2\ RAlH_2 \rightarrow R_2AlH + AlH_3 \qquad (23)$$

$$AlH_3 \rightarrow Al + 3/2\ H_2 \qquad (24)$$

The decomposition of $HMgAlH_3R$ in the above manner is not surprising in view of the results of Ziegler and Holzkamp.[10] These workers attempted

to distill $Mg[Al(C_2H_5)_4]_2$ but instead obtained $Al(C_2H_5)_3$ by distillation leaving behind the involatile $Mg(C_2H_5)_2$ (eq. 25).

$$Mg[Al(C_2H_5)_4]_2 \xrightarrow{\Delta} Al(C_2H_5)_3 + Mg(C_2H_5)_2 \qquad (25)$$

RMgBH$_4$ Pyrolysis. Ethylmagnesium borohydride was obtained as the THF solvate and was dissolved in 100 ml of heavy mineral oil. This solution was heated slowly to a temperature of 170°. At this point a gas was evolved and a solid formed. The solid obtained was filtered and washed with benzene. Elemental analysis of this solid gave a Mg:H ratio of 1.0:3.74 with no ethane present. The infrared spectrum of the solid exhibited absorption bands at 2270 and 2380 cm^{-1} characteristic of $Mg(BH_4)_2$ as the THF solvate. X-ray powder pattern analysis of the solid exhibited strong lines characteristic of magnesium hydride.

The pyrolysis of sec-butylmagnesium borohydride was attempted since the sec-butyl group is more susceptible to olefin elimination at a lower temperature. Sec-butylmagnesium borohydride as the diethyl ether solvate was dissolved in octane and heated to 80° under vacuum. A solid was obtained that exhibited lines in its X-ray powder pattern characteristic of a mixture of magnesium hydride and $Mg(BH_4)_2$.

Magnesium aluminum hydride as the monotetrahydrofuran solvate was heated to 145° until weight loss was constant. The resulting solid was gray in color and its X-ray powder pattern showed lines for MgH_2 and aluminum metal only.

$HMgAlH_3R$ Hydrogenolysis. - The hydrogenolysis of $HMgAlH_3(n\text{-}C_4H_9)$ in diethyl ether was carried out at 3000 psi hydrogen at 50°. The solution was filtered and the elemental analysis of the filtrate gave a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate gave bands in the Al-C stretching region at 670 cm^{-1} and a shoulder at 700 cm^{-1}, also a band at 1680 cm^{-1}. This combination of absorption bands is characteristic of $[AlR_2H_2]^-$ compounds. The solid obtained from this filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3:2.63. The infrared spectrum of the solid corresponded to magnesium hydride, however, no bands in the Al-H stretching region were observed. The X-ray powder pattern corresponded to magnesium hydride and aluminum metal. Although hydrogenolysis of an $RMgAlH_4$ compound would be expected to product $HMgAlH_4$ or a mixture of MgH_2 and $Mg(AlH_4)_2$, only MgH_2 was detected.

The hydrogenolysis of $HMgAlH_3R$ compounds appears to follow a course similar to the pyrolysis of this class of compounds. That is, the formation of MgH_2 and $RAlH_2$ followed by disproportionation of the $RAlH_2$ to R_2AlH and AlH_3. The R_2AlH could then react with the MgH_2 formed to give $Mg(AlR_2H_2)_2$. The AlH_3 would decompose to hydrogen and aluminum metal as indicated by the powder pattern of the solid.

$$HMgAlH_3 \xrightarrow{\Delta} MgH_2 + RAlH_2 \qquad (26)$$

$$2\ RAlH_2 \rightarrow R_2AlH + AlH_3 \qquad (27)$$

$$AlH_3 \rightarrow Al + 3/2\ H \qquad (28)$$

$$2\ R_2AlH + MgH_2 \rightarrow Mg(AlR_2H_2)_2 \qquad (29)$$

RMgBH$_4$ Hydrogenolysis. - The results of the hydrogenolysis of sec-butylmagnesium borohydride in both diethyl ether and benzene are straight forward. Reaction at 2000 psi hydrogen at 50° produced a white solid that had an infrared spectrum corresponding to magnesium hydride, however, no bands in the boron-hydrogen stretching region were observed. The X-ray powder pattern gave strong lines corresponding to pure magnesium hydride. The weight of the solid obtained corresponded to a quantitative yield of magnesium hydride. The filtrate from this reaction exhibited infrared bands at 2450 and 2220 cm^{-1} characteristic of $Mg(BH_4)_2$ as the diethyl ether solvate.

$$2(s\text{-}C_4H_9MgBH_4) \xrightarrow{H_2} MgH_2 + Mg(BH_4)_2 + C_4H_{10} \qquad (30)$$

When the reaction was carried out in benzene, similar results were obtained, i.e., a solid consisting of magnesium hydride and magnesium borohydride (as the ether solvate) in solution was formed.

In an attempt to learn something of the nature of sec-butylmagnesium borohydride in solution, molecular association measurements in diethyl ether were carried out. The association was found to increase steadily from i = 1.23 at 0.066 molal to i = 1.45 at 0.31 molal. It is clear that hydrogenolysis of this compound does not produce hydridomagnesium borohydride but instead a mixture of magnesium hydride and magnesium borohydride. This result also establishes the point that magnesium hydride and magnesium borohydride will not redistribute in solution to yield hydridomagnesium borohydride.

$RMgBH_4$ + MH. - Ethylmagnesium borohydride in diethyl ether was allowed to react with tri-n-butyltin hydride in a 1:1 mole ratio for several days. At the end of this time the mixture was filtered. The infrared spectrum of the solution showed bands characteristic of unreacted $EtMgBH_4$ and Bu_3SnH. The analysis of the resulting solid gave a Mg:H ratio of 1.0:2.3. The X-ray powder pattern of this solid corresponded to that of magnesium hydride.

In another experiment s-butylmagnesium borohydride in diethyl ether was also allowed to react with tri-n-butyltin hydride in a 1:1 mole ratio. Infrared spectra of the supernatant solution were taken at various intervals. The spectra indicated the disappearance of the Sn-H band at 1800 cm^{-1} and the Mg-C stretching band at 535 cm^{-1}. When these bands had disappeared completely the solution was filtered. The solid obtained by this filtration gave a Mg:H ratio of 1.0:1.89. Its infrared spectraum showed no bands due to B-H stretching but did show bands characteristic of magnesium hydride. Infrared analysis of the reaction filtrated indicated the presence of $Mg(BH_4)_2$.

$$s\text{-}C_4H_9MgBH_4 + (n\text{-}C_4H_9)_3SnH \rightarrow 1/2\ MgH_2 + 1/2\ Mg(BH_4)_2 + (n\text{-}C_4H_9)_3Sn(s\text{-}C_4H_9) \qquad (31)$$

$HMgAlH_3R$ + MH. - Tri-n-butyltin hydride was allowed to react in a 1:1 mole ratio with $HMgAlH_3(C_2H_5)$ in ether and in a separate experiment with $HMgAlH_3(n\text{-}C_4H_9)$. In both cases a trace amount of solid of indefinite composition was formed within a few minutes of initiation of the reaction. However, the amount of this solid did not increase even after stirring for several days. The infrared spectrum of the solution showed a mixture of unreacted Bu_3SnH and $HMgAlH_3(C_2H_5)$. The infrared spectrum of the solution

did not change even after stirring for several days. The conclusion is that the $(C_4H_9)SnH$ does not react with $HMgAlH_3(C_2H_5)$ or $HMgAlH_3(n\text{-}C_4H_9)$.

Neuman and coworkers[11] in the examination of the reaction of

(11) W. P. Neuman, H. Niermann, and B. Schneider, Angew. Chem. Internat. Ed. 2, 547 (1963).

trialkyltin hydrides with aluminum alkyls found that ethers and tertiary amines inhibit the reaction. They conclude that the electron deficient state of the aluminum is important in the exchange. Since in the tetrahydridoaluminate compounds the aluminum is no longer electron deficient, it is perhaps not surprising that the reaction between $(C_4H_9)_3SnH$ and $HMgAlH_3R$ compounds does not proceed. Van Der Kerk and coworkers[12] in their

(12) H. M. J. C. Creemers, J. G. Noltes, and G. J. M. Van Der Kerk, J. Organometal. Chem., 14, 217 (1968).

examination of the reaction between $(C_6H_5)_3SnH$ and $(C_2H_5)MgBr\cdot N(C_2H_5)_3$ reported that instead of getting hydrogen-alkyl exchange, ethane was evolved and a compound with a tin-magnesium bond was formed. It should be emphasized that in none of the reactions between R_3SnH and either $HMgAlH_3R$ or $RMgBH_4$ compounds was any gas evolved.

It was hoped that by reacting $HMgAlH_3R$ compounds with a large excess of $LiAlH_4$ or $NaAlH_4$, alkyl-hydrogen exchange would take place resulting in the precipitation of $HMgAlH_4$ from solution. However, in a series of experiments it was shown that little reaction occurs and that most of the starting materials are recovered unreacted.

$$LiAlH_4 + HMgAlH_3(C_2H_5) \not\longrightarrow HMgAlH_4 + LiAlH_3(C_2H_5) \qquad (32)$$

A further attempt to prepare $HMgAlH_4$ by alkyl-hydrogen exchange involves the reaction of diethylaluminum hydride with $HMgAlH_3(n\text{-}C_4H_9)$ in a 1:1 mole ratio in diethyl ether. No solid was formed after stirring the solution for several days. The diethyl ether was then removed under vacuum and the solid obtained was heated under vacuum to 80°. At this point a clear colorless liquid distilled. The analysis of this distillate after diethyl ether was added gave an Al:H ratio of 1.1:1.0. The infrared spectrum of the solution gave a sharp band at 1755 cm^{-1} indicating the presence of $(C_2H_5)_2AlH$. The solid remaining after the distillation was complete gave a Mg:Al:H ratio of 1.5:1.0:4.5. The X-ray powder pattern of the solid showed lines characteristic of $HMgAlH_3(n\text{-}C_4H_9)$, MgH_2 and aluminum metal.

In this reaction a complex may have been formed between $(C_2H_5)_2AlH$ and $HMgAlH_3(n\text{-}C_4H_9)$ which upon heating decomposed again to $(C_2H_5)_2AlH$ and $HMgAlH_3(n\text{-}C_4H_9)$. The low aluminum analysis of the solid as well as the presence of aluminum metal and MgH_2 in the powder pattern may be due to a decomposition of $HMgAlH_3(n\text{-}C_4H_9)$ similar to that seen in the pyrolysis experiments.

$$(C_2H_5)AlH + HMgAlH_3(n\text{-}C_4H_9) \rightarrow [(C_2H_5)_2AlH\cdot HMgAlH_3(n\text{-}C_4H_9) \xrightarrow{\Delta} (C_2H_5)_2AlH + HMgAlH_3(n\text{-}C_4H_9)$$

Diethylmagnesium was allowed to react with aluminum hydride in THF in a mole ratio of 3:5. It was expected that $Al(C_2H_5)_3$ and $HMgAlH_4$ would be formed according to equation 34. However, no solid formed initially.

$$3\ Mg(C_2H_5)_2 + 5\ AlH_3 \begin{cases} \not\rightarrow\ 2\ Al(C_2H_5)_3 + 3\ HMgAlH_4 \\ \rightarrow\ 2(C_2H_5)_2AlH + 3\ HMgAlH_3(C_2H_5) \end{cases} \qquad (34)$$

The tetrahydrofuran solvent was removed under vacuum and hexane added. The hexane solution was then filtered and the analysis of the filtrate gave an Al:H ratio of 1.0:2.04. The analysis of the resulting solid gave an Al:H ratio of 1.0:3.5. This indicates that equation 34 is not followed but that the alkyl groups are statistically distributed between the two aluminum compounds.

When hydridomagnesium tetraethylaluminate in THF was allowed to react with an excess of sodium aluminum hydride, no precipitate formed after stirring for several days. Here again, there is probably a statistical redistribution of the alkyl groups among the aluminum atoms.

$$HMgAl(C_2H_5)_4 + NaAlH_4 \not\longrightarrow HMgAlH_4 + NaAl(C_2H_5)_4 \qquad (35)$$

<u>$Mg(AlH_4)_2$ + L.</u> - Sodium hydride was allowed to react with $Mg(AlH_4)_2 \cdot 4THF$ in THF solution. The solution was stirred for several days and then filtered. The infrared spectrum of the filtrate was identical with an independent sample of $NaAlH_4$. The infrared spectrum of the solid showed it to be a mixture of MgH_2 and $Mg(AlH_4)_2 \cdot 4THF$. Equations 36 and 37 are presented to describe the most probable reaction path.

$$NaH + Mg(AlH_4)_2 \rightarrow NaAlH_4 + HMgAlH_4 \qquad (36)$$

$$2\ HMgAlH_4 \rightarrow MgH_2 + Mg(AlH_4)_2 \qquad (37)$$

We have previously found[13] that trimethylamine abstracts AlH_3

(13) J. A. Dilts and E. C. Ashby, Inorg. Chem., 9, 855 (1970).

from $Mg(AlH_4)_2$ in 42% yield after ten days in a sealed tube. In an attempt to determine if the AlH_3 abstraction produces $HMgAlH_4$ as an intermediate product, we allowed trimethylamine to react with $Mg(AlH_4)_2$ in a sealed tube for ten days. At the end of this time we recovered $AlH_3 \cdot 2\ NMe_3$ in 95% yield. The solid remaining was shown by elemental, infrared and X-ray powder pattern analysis to be MgH_2.

$$Mg(AlH_4)_2 + N(CH_3)_3 \begin{cases} \not\rightarrow\ HMgAlH_4 + AlH_3 \cdot N(CH_3)_3 \\ \rightarrow\ MgH_2 + 2[AlH_3 \cdot 2N(CH_3)_3] \end{cases} \qquad (38)$$

In an attempt to desolvate $Mg(AlH_4)_2 \cdot THF$, this compound was heated to 140° until all the THF had been removed. Desolvated $Mg(AlH_4)_2$ was desired so that the thermal decomposition of this compound could be studied in an effort to effect partial pyrolysis of $Mg(AlH_4)_2$ to $HMgAlH_4$, aluminum and hydrogen. However, the solid obtained from the desolvation was shown by X-ray powder diffraction to contain MgH_2 and aluminum metal.

$$Mg(AlH_4)_2 \xrightarrow{\Delta} \begin{cases} \not\rightarrow\ HMgAlH_4 + Al + 1/2\ H_2 \\ \rightarrow\ MgH_2 + 2\ Al + 3\ H_2 \end{cases} \qquad (39)$$

$\underline{Mg(BH_4)_2 + L.}$ - Sodium hydride was allowed to react with $Mg(BH_4)_2$ in diethyl ether in a mole ratio of 1:1. After stirring for several days

the solution was filtered. The infrared spectrum of the filtrate was identical with an independent sample of $Mg(BH_4)_2$. The X-ray powder pattern showed lines corresponding to sodium borohydride and magnesium hydride. This indicates that any $HMgBH_4$ formed via borane extraction disproportionated to MgH_2 and $Mg(BH_4)_2$.

$$NaH + Mg(BH_4)_2 \rightarrow NaBH_4 + HMgBH_4 \quad (40)$$

$$2\ HMgBH_4 \rightarrow MgH_2 + Mg(BH_4)_2 \quad (41)$$

$\underline{MgH_2 + AlH_3}$. - Magnesium hydride was allowed to react with $AlH_3 \cdot 2THF$ in benzene. The resulting solution was filtered and the filtrate showed weak bands at 1735, 910 and 750 cm^{-1}. These bands are characteristic of $Mg(AlH_4)_2 \cdot 4THF$ which is slightly soluble in tetrahydrofuran. The infrared spectrum of the solid obtained from this filtration showed bands corresponding to $Mg(AlH_4)_2 \cdot 4THF$ and MgH_2. The X-ray powder pattern of the solid showed lines corresponding to $Mg(AlH_4)_2 \cdot 4THF$. It is very probable that in this case $HMgAlH_4$ is formed. However, it is not clear whether the $Mg(AlH_4)_2$ actually isolated in this reaction is a result of the disproportionation of $HMgAlH_4$ or simply a result of the further reaction of $HMgAlH_4$ with $AlH_3 \cdot 2THF$. Magnesium hydride was found not to react with bis-trimethylamine alane in benzene solution.

$$MgH_2 + AlH_3 \rightarrow HMgAlH_4 \xrightarrow{AlH_3} Mg(AlH_4)_2 \quad (42)$$

Although no specific reaction between MgH_2 and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was studied, it is clear from the results of a number of the reactions described in this paper that MgH_2 does not redistribute

with either $Mg(AlH_4)_2$ to give $HMgAlH_4$ or with $Mg(BH_4)_2$ to give $HMgBH_4$.

To summarize, we have investigated seven general methods for preparing $HMgAlH_4$ (eqs. 3-9). In none of these cases was $HMgAlH_4$ or $HMgBH_4$ isolated. Instead, a physical mixture of MgH_2 and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was obtained.

In all probability, if $HMgAlH_4$ or $HMgBH_4$ were stable compounds some of the reactions carried out in this study should have produced these compounds. We have concluded, therefore, that $HMgAlH_4$ and $HMgBH_4$ are unstable and disproportionate to MgH_2 and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ in ether solvents.

Acknowledgement. - We are indebted to the Office of Naval Research (Contract No. N000 14-67-A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

Concerning the Reactions of Lithium and Sodium Aluminum Hydride with Grignard Reagents in Ether Solvents

E. C. Ashby and R. D. Schwartz

Abstract

The reaction of lithium aluminum hydride with n-butylmagnesium bromide was found to proceed according to the following sequence of reactions:

$$LiAlH_4 + 6\ n\text{-}C_4H_9MgBr \rightarrow 2\ n\text{-}C_4H_9MgBr + 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \rightarrow 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 3\ n\text{-}C_4H_9MgBr \rightarrow MgH_2 + LiBr + 1/2\ MgBr_2 + BrMgAlH(n\text{-}C_4H_9)_3$$

$$LiAlH_4 + 2\ n\text{-}C_4H_9MgBr \rightarrow MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 + LiBr$$

$$MgH_2 + BrMgAlH_2(n\text{-}C_4H_9) \rightarrow BrMgAlH_4(n\text{-}C_4H_9)_2$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \rightarrow n\text{-}C_4H_9MgAlH_4 + LiBr$$

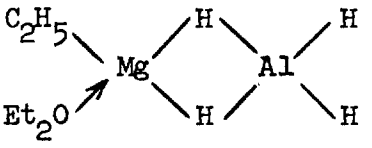
$$n\text{-}C_4H_9MgAlH_4 \rightarrow HMgAlH_3(n\text{-}C_4H_9)$$

The stability of $HMgAlH_3R$ compounds was found to be dependent on the alkyl group. When $R=C_2H_5$ and $n\text{-}C_4H_9$ the $HMgAlH_3R$ compounds are stable, however, when $R=CH_3$, C_6H_5, or $s\text{-}C_4H_9$, the $HMgAlH_3R$ compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether.

Introduction

Wiberg and Strebel[1] have reported that addition of lithium aluminum hydride to ethylmagnesium chloride in diethyl ether yields a soluble compound of empirical formula $C_2H_5MgAlH_4$. The structure assigned to this compound is shown by I, however, no spectral data were reported to verify this structure.

(1) P. Strebel, Ph.D. Dissertation, University of Munich, 1958.



(I)

The formation of $C_2H_5MgAlH_4$ can be looked upon as resulting from a simple metathetical exchange reaction involving the formation of stable LiCl as a by-product.

$$C_2H_5MgCl + LiAlH_4 \rightarrow C_2H_5MgAlH_4 + LiCl \qquad (1)$$

If the product of this reaction has the structure shown in I, then this class of compounds represents a good starting point for the preparation of $HMgAlH_4$ by hydrogenolysis (eq. 2), since we have already demonstrated the ease of hydrogenolysis of R-Mg to H-Mg compounds especially when R=i-C_3H_7 or s-C_4H_9.[2]

$$RMgAlH_4 \xrightarrow{H_2} HMgAlH_4 + RH \qquad (2)$$

(2) W. E. Becker and E. C. Ashby, J. Org. Chem., 20, 954 (1964). E. C. Ashby, R. A. Kovar and K. Kawakami, Inorg. Chem., 9, 317 (1970). E. C. Ashby, R. A. Kovar and R. Arnott, J. Amer. Chem. Soc., 92, 2182 (1970).

In 1956 Rice[3] reported that when phenylmagnesium bromide was

(3) H. J. Rice and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ONR-494(04) 1956.

allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 6:1, the resulting product exhibited the empirical formula $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$. When the ratio of Grignard reagent to lithium aluminum hydride was 10:1, a product of empirical formula $C_6H_5MgBr \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$ was isolated. These compounds were reported to be soluble in benzene and insoluble in diethyl ether. Rice envisioned the reactions as proceeding according to eq. 3. At the higher Grignard

$$4\ C_6H_5MgBr + LiAlH_4 \rightarrow 4\ C_6H_5MgH + LiBr + AlBr_3 \qquad (3)$$

to lithium aluminum hydride ratios, C_6H_5MgH could complex with the excess $(C_6H_5)_2Mg$ or C_6H_5MgBr in solution to give the products reported.

Because of our desire to prepare $HMgAlH_4$, attempts were made to prepare $RMgAlH_4$ compounds according to the method of Wiberg and Strebel. However, hydrogenolysis of the so called $RMgAlH_4$ compounds did not produce $HMgAlH_4$. Further inspection of the infrared spectra of the $RMgAlH_4$ compounds showed the absence of absorption in the Mg-C stretching region (500-550 cm^{-1}) which would be expected if $RMgAlH_4$ had the structure shown in (I). Furthermore, in the reaction reported by Wiberg and Strebel all

of the reactive magnesium species in solution should be considered (R_2Mg and RMgX). Since R_2Mg is the more reactive of the R-Mg species in solution, it is not clear that all of the reaction with $LiAlH_4$ should proceed through the RMgX species. In addition, it would appear that the hydrogen and R groups could exchange readily in a system such as $RMgAlH_4$ such that rearrangement of $RMgAlH_4$ to $HMgAlH_3R$ might take place readily. Of the two compounds, $HMgAlH_3R$ would be expected to be the more stable since hydrogen would tend to reside on the more electropositive metal (magnesium).

Our previous study of the reaction of $LiAlH_4$ with magnesium halides[4] indicates that a metathetical exchange reaction involving the

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(4) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

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formation of lithium halide and $Mg\text{-}AlH_4$ compounds (eq. 4) takes place

$$LiAlH_4 + MgBr_2 \rightarrow BrMgAlH_4 + LiBr \qquad (4)$$

rather than the type reaction reported by Rice (eq. 3) in which the AlH_4 group does not maintain its integrity.

Considering these differences in the prior art concerning such a fundamental reaction and our desire to prepare $RMgAlH_4$ compounds, we decided to study the reactions of alkali metal aluminum hydrides with Grignard reagents in ether solvents in detail in order to determine the exact course of this reaction.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[5] or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

(5) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer Model 621 High Resolution Infrared Spectrophotometer. Cesium Iodide cells were used. X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Triply sublimed magnesium was obtained from Dow Chemical Co. The magnesium was washed with diethyl ether and dried under vacuum prior to use. Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Lithium aluminum hydride solutions in diethyl ether were prepared as described previously.[4] Sodium aluminum hydride was recrystallized from diethyl ether - THF mixtures.

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine and titrating the magnesium with EDTA. Hydridic hydrogen was measured by hydrolyzing a weighed sample on a high vacuum line and transferring the gas to a calibrated bulb via a Topler pump after passing the gas through a liquid nitrogen trap.

The experimental procedure used in carrying out several typical reactions are now reported.

Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Chloride in Diethyl Ether. - To 45.06 mmoles of lithium aluminum hydride was added 150 ml diethyl ether. To this solution was added 28.71 ml of n-butylmagnesium chloride in diethyl ether (0.5642 M). The solution was stirred overnight at room temperature. The solution was filtered and 1.6661 gm of solid isolated which gave on analysis: Cl:74.83, Mg:2.98, Al:0.99. The clear filtrate gave the following analysis: Mg:Al:Cl, 1.0:1.02:0.1. The solution contained 95% of the initial amount of magnesium. The infrared spectrum of the filtrate showed bands at 1760 cm^{-1} (broad), 720 cm^{-1} and 680 cm^{-1} (sh). In a separate experiment the solvent was removed from the filtrate and the resulting solid gave an infrared spectrum with bands at 1760 cm^{-1} (broad) and 720 cm^{-1}. The X-ray powder pattern of the solid showed no lines for magnesium hydride. When this solid was dissolved in THF, the resulting infrared spectrum gave bands at 1700, 790, and 755 cm^{-1}.

Reaction of Lithium Aluminum Hydride with sec-Butylmagnesium Chloride in Diethyl Ether. - To 10 ml s-butylmagnesium chloride in diethyl ether (2.41 M) was added 14.19 ml of lithium aluminum hydride in diethyl ether (1.698 M). The solution was stirred overnight. The solution was filtered and 1.1582 gm of solid was isolated. The solid on analysis gave a Mg:Al:Cl ratio of 1.0:0.02:0.85. The amount of magnesium contained in the solid represented 65% of the initial magnesium. The infrared spectrum of this solid showed it to contain magnesium hydride. Analysis of the solution gave a Mg:Al ratio of approximately 2.0:3.0.

Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide at a Mole Ratio of 1:4. - To 100 ml of n-butylmagnesium bromide in diethyl ether (0.5786 M) was added 6 ml of lithium aluminum hydride in ether (2.424 M). The solution was stirred overnight and then filtered. Elemental analysis of the solid gave a Mg:H ratio of 1.0:1.86. The amount of magnesium in the solid corresponded to 46.2% of the initial amount of magnesium. The infrared spectrum and X-ray powder pattern of the solid corresponded to MgH_2. The infrared spectrum of the filtrated showed a band at 670 cm^{-1} and a shoulder at 615 cm^{-1}. No bands were observed in the Al-H stretching region (2000-1600 cm^{-1}). The solvent was then removed from the filtrate under vacuum at room temperature. Benzene was added to the resulting solid and the mixture stirred overnight. The mixture was then filtered and the analysis of the filtrate gave a Br:Mg:Al:Butane ratio of 1.0:0.98:1.03:4.28. No hydrogen or lithium were detected in the filtrate and the amount of aluminum in the benzene solution corresponded to 92.54% of the initial amount of aluminum.

In a separate experiment n-butylmagnesium bromide was allowed to react with lithium aluminum hydride in a mole ratio of 4:2.25. At this point all the solid formed initially had redissolved. The infrared spectrum of the solution showed a broad band at 1710 cm^{-1}. The solvent was then removed under vacuum at room temperature and benzene was added. This mixture was then stirred overnight and filtered. The analysis of the filtrate gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This represents 98.4% of the initial amount of aluminum.

Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide in Tetrahydrofuran. - To 43.4 mmoles of n-butylmagnesium bromide was added 75 ml of THF. To the resulting clear solution was added in a dropwise fashion 40.54 ml of $LiAlH_4$ in THF (1.070 **M**). No solid was formed during the addition and the solution was allowed to stir overnight. The infrared spectrum of the resulting clear solution corresponded to $HMgAlH_3(n\text{-}C_4H_9)$.

Infrared Study of the Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide in Diethyl Ether. A 0.4 M solution of n-butylmagnesium bromide in diethyl ether was placed in a one-neck round bottom flask equipped with a side-arm with stopcock. A 2.424 **M** solution of $LiAlH_4$ was added to this solution in increments via syringe. After each addition the solution was stirred for one-half hour and then any solid formed was allowed to settle. A sample of the supernatant solution was then withdrawn via syringe for infrared analysis. At a Grignard to hydride ratio of 1.0:0.0 the following bands were observed: 895, 780, and 540 cm^{-1}. At a Grignard to hydride ratio of 6:1 the 895 and 780 cm^{-1} bands remain the same, but the 540 cm^{-1} band has decreased in intensity and new bands

at 670 with a shoulder at 620 cm^{-1} appear. A solid formed at this ratio. At a Grignard to hydride ratio of 4:1 the 895 and 780 cm^{-1} bands are unchanged but the 540 cm^{-1} band has disappeared and the 670 and 620 cm^{-1} bands have increased in intensity and more solid has formed. At a Grignard to hydride ratio of 3:1 the 895 and 780 bands are the same, the 670 and 620 bands have decreased somewhat in intensity but a new band has appeared at 1620 cm^{-1}. The amount of solid doesn't seem to have changed. At a Grignard to hydride ratio of 2:1, the 895 and 780 cm^{-1} bands are unchanged, however, the 670 and 620 cm^{-1} have disappeared and a band at 705 cm^{-1} has appeared. The band at 1620 cm^{-1} has disappeared, however, intense band at 1710 cm^{-1} has appeared. At this ratio all the solid has redissolved. At a Grignard reagent:hydride ratio of 1:1, all the solid is still in solution and the solution spectrum show bands at 1760, 895, 780, and 680 cm^{-1}.

Preparation of Isopropoxymagnesium Bromide. - To 25 ml of ethyl magnesium bromide in ether (3.016 M) was added 200 ml of ether. The solution was then cooled to 0° and 5.77 ml of neat isopropanol was added slowly. A gas was given off and the solution stirred overnight. The analysis of the solution gave a Mg:Br ratio of 1.0:1.1.

Reaction of Lithium Aluminum Hydride with Isopropoxymagnesium Bromide. - To 75 ml of isopropoxymagnesium bromide in diethyl ether (0.2059 M) was added 15.7 ml of lithium aluminum hydride in ether (0.9811 M). The solution was then stirred overnight and filtered. The analysis of the filtrate gave a Mg:Al:Br ratio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained from the filtration corresponded

to magnesium hydride and showed no bands due to Al-H stretching.

Preparation of di-n-Butylaminomagnesium Chloride. - To 30 ml of ethylmagnesium chloride in ether (1.149 m) was added 70 ml ether. To this solution was then added 5.8 ml di-n-butylamine. The solution was then stirred overnight during which time no precipitate formed.

Results and Discussion

An infrared study of the reaction between n-butylmagnesium bromide and lithium aluminum hydride shows that the reaction proceeds by a stepwise exchange of alkyl groups from magnesium to aluminum and an exchange of hydrogen from aluminum to magnesium, as shown in equations 5-11. Although HMgBr would be an initial product, this compound is known to disproportionate rapidly to MgH_2 and $MgBr_2$ in ether solution.

$$LiAlH_4 + 6\ n\text{-}C_4H_9MgBr \rightarrow 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 + 2\ n\text{-}C_4H_9MgBr \quad (5)$$

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \rightarrow 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 \quad (6)$$

$$LiAlH_4 + 3\ n\text{-}C_4H_9MgBr \rightarrow 3/2\ MgH_2 + LiBr + 1/2\ MgBr_2 + BrMgAl(n\text{-}C_4H_9)_3H \quad (7)$$

$$LiAlH_4 + 2\ n\text{-}C_4H_9MgBr \rightarrow MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 + LiBr \quad (8)$$

$$MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 \rightarrow BrMgAlH_4(n\text{-}C_4H_9)_2 \quad (9)$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \rightarrow LiBr + n\text{-}C_4H_9MgAlH \quad (10)$$

$$n\text{-}C_4H_9MgAlH_4 \rightarrow HMgAlH_3(n\text{-}C_4H_9) \quad (11)$$

At a ratio of 1.0 $LiAlH_4$ to 6 n-C_4H_9MgBr (eq. 5) the infrared band at 540 cm^{-1} characteristic of n-C_4H_9MgBr[6] has decreased in intensity

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(6) n-C_4H_9MgBr is used throughout this paper to represent the Grignard reagent (n-butylmagnesium bromide). If reference is made to the distinct RMgX species then the terminology "n-C_4H_9MgBr species" is used.

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indicating that some of the Grignard reagent has reacted. The band at 670 cm^{-1} with a shoulder at 620 cm^{-1} is characteristic of the AlR_4^- group.[7]

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(7) E. C. Ashby and R. G. Beach, Inorg. Chem., 9, 2300 (1970).

At a ratio of 1.0 $LiAlH_4$ to 4.0 n-C_4H_9MgBr (eq. 6) the band at 540 cm^{-1}, characteristic of n-C_4H_9MgBr[6] has disappeared but the bands at 670 cm^{-1} and 620 cm^{-1} (sh) have increased in intensity. This indicates that all the Grignard reagent has reacted. The solid which began to form in the 6:1 case has now increased. In a separate experiment the solid was isolated by filtration and shown be elemental analysis, X-ray powder pattern and infrared analysis to be MgH_2. The amount of MgH_2 isolated corresponded to a 92.4 percent yield according to equation 6. The solvent was then removed from the filtrate and the solid thus obtained was stirred in benzene overnight. The mixture was then filtered and the solution analyzed. The analysis indicated the presence of a compound of empirical formula $BrMgAl(n\text{-}C_4H_9)_4$. The amount of aluminum in the solution indicated a yield of $BrMgAl(n\text{-}C_4H_9)_4$ of 92 percent according to equation 6.

The products of equation 6 can be envisioned as resulting from two reaction paths. The first path involves reaction of $LiAlH_4$ with the C-Mg

bond of the Grignard reagent according to equation 12.

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \rightarrow LiAl(n\text{-}C_4H_9)_4 + 4\ HMgBr \longrightarrow 2\ MgH_2 + 2\ MgBr_2 \qquad (12)$$

The $LiAl(n\text{-}C_4H_9)_4$ thus produced can then react with $MgBr_2$ to yield $BrMgAl(n\text{-}C_4H_9)_4$ according to equation 13.

$$LiAl(n\text{-}C_4H_9)_4 + MgBr_2 \rightarrow LiBr + BrMgAl(n\text{-}C_4H_9)_4 \qquad (13)$$

The second path involves the reaction of $LiAlH_4$ with the Mg-Br bond of the Grignard reagent according to equation 14. The $n\text{-}C_4H_9MgAlH_4$ formed rearranges to $HMgAlH_3(n\text{-}C_4H_9)$ which then reacts with the remaining Grignard reagent according to equation 16 to yield $HMgAl(n\text{-}C_4H_9)_4$, MgH_2 and $MgBr_2$. The $HMgAl(n\text{-}C_4H_9)_4$ then reacts with $MgBr_2$ according to equation 17.

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \rightarrow LiBr + n\text{-}C_4H_9MgAlH_4 + 3\ n\text{-}C_4H_9MgBr \qquad (14)$$

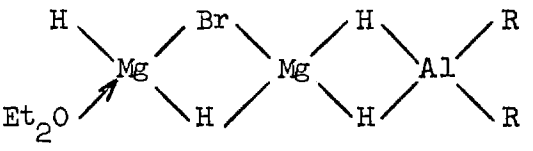
$$n\text{-}C_4H_9MgAlH_4 \rightarrow HMgAlH_3(n\text{-}C_4H_9) \qquad (15)$$

$$HMgAlH_3(n\text{-}C_4H_9) + 3\ n\text{-}C_4H_9MgBr \rightarrow HMgAl(n\text{-}C_4H_9)_4 + 1.5\ MgH_2 + 1.5\ MgBr_2 \qquad (16)$$

$$HMgAl(n\text{-}C_4H_9)_4 + MgBr_2 \rightarrow BrMgAl(n\text{-}C_4H_9)_4 + 0.5\ MgH_2 + 0.5\ MgBr_2 \qquad (17)$$

At a ratio of 1.0 $LiAlH_4$ to 3.0 $n\text{-}C_4H_9MgBr$ (eq. 7) the bands at 670 cm^{-1} and 620 cm^{-1} decreased in intensity somewhat and a new band at 1620 cm^{-1} has appeared. The combination of bands between 600-700 cm^{-1} and one at approximately 1600 cm^{-1} was shown earlier[7] to be characteristic of $[AlR_3H]^-$ compounds.

At a ratio of 1.0 $LiAlH_4$ to 2.0 n-C_4H_9MgBr (eq. 8) the bands at 670 and 620 cm^{-1} disappeared and a band at 705 cm^{-1} appeared. Also, the band at 1620 cm^{-1} disappeared, however, an intense band at 1710 cm^{-1} appeared. This combination of bands around 1700 cm^{-1} and 700 cm^{-1} has been shown[7] to be characteristic of the $[AlR_2H_2]^-$ group. Also, at this ratio the MgH_2 noted above has all redissolved. In a separate experiment $LiAlH_4$ was added to n-C_4H_9MgBr in a ratio of 2.25:4.0. The solvent was removed under vacuum and the resulting solid extracted with benzene. Analysis of the benzene solution after filtration gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This ratio can be rationalized as representing a compound of empirical formula $BrMg_2AlH_2(n\text{-}C_4H_9)_2$. A reasonable structure for this compound is shown below:



(II)

At a ratio of 1.0 $LiAlH_4$ to 1.0 n-C_4H_9MgBr (eq. 10) the solution is clear. The infrared spectrum of the solution shows bands at 1760 cm^{-1} and 720 cm^{-1}. This combination of bands has been shown[7] to be characteristic of $[AlH_3R]$ compounds.

When n-butylmagnesium chloride was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 1:1, a solid was obtained which was shown by elemental analysis and X-ray powder pattern analysis to be lithium chloride. Analysis of the filtrate gave aMg:Al ratio of 1.0:1.02 and the amount of magnesium in solution represented

95% of the original magnesium. The infrared spectrum of the filtrate showed broad bands at 1760 and 720 cm^{-1} with a shoulder at 680 cm^{-1}. No bands were observed in the Mg-C stretching region (500-535 cm^{-1}). Lithium monoethylaluminate exhibits a broad absorption at 1740 cm^{-1} with a shoulder at 700 cm^{-1}. This band is very similar in shape and position to the Al-H stretching band at 1760 cm^{-1} exhibited by $HMgAlH_3(n\text{-}C_4H_9)$. Thus, we have concluded that the alkyl group is bonded to the aluminum and not magnesium.

In a separate experiment $LiAlH_4$ was allowed to react with $n\text{-}C_4H_9MgBr$ in a 1.0:1.0 ratio. The solution spectrum was identical to that observed earlier in the infrared study when the ratio of $LiAlH_4$:$n\text{-}C_4H_9MgBr$ was 1:1. The solvent was removed from the reaction mixture and the X-ray powder pattern showed lines corresponding to LiBr plus other lines corresponding to the $HMgAlH_3(n\text{-}C_4H_9)$ isolated from the 1:1 addition of $n\text{-}C_4H_9MgCl$ to $LiAlH_4$ discussed above.

When $HMgAlH_3(n\text{-}C_4H_9)$ was dissolved in THF the major absorption bands in the infrared shifted to 1700, 790 and 755 cm^{-1}. Still in THF no bands are observed in the 500-535 cm^{-1} region characteristic of a C-Mg compound, so that the butyl group is also presumed to be attached to aluminum in THF solution.

When lithium aluminum hydride was allowed to react with ethylmagnesium chloride in diethyl ether at a mole ratio of 1:1, a solution was obtained which after filtration was shown by elemental analysis to have a Cl:Mg:Al ratio of 0.1:1.00:1.05. The infrared spectrum of the solution exhibited an absorption band at 1750 cm^{-1} with a shoulder at 1685 cm^{-1}. It is important to note that if the reaction was allowed

to become too vigorous, the initially formed $HMgAlH_3(C_2H_5)$ disproportionated to MgH_2 and $Mg[AlH_3(C_2H_5)]_2$. In the case of the formation of $HMgAlH_3(n\text{-}C_4H_9)$, no evidence of disproportionation was observed even under reflux conditions.

$$LiAlH_4 + C_2H_5MgCl \xrightarrow[\text{temperature}]{\text{room}} LiCl + HMgAlH_3(C_2H_5) \quad (18)$$

$$LiAlH_4 + C_2H_5MgCl \xrightarrow{\text{ether reflux}} LiCl + 1/2\ MgH_2 + 1/2\ Mg(AlH_3C_2H_5)_2 \quad (19)$$

We attempted to prepare methylmagnesium aluminum hydride by the reaction of sodium aluminum hydride with methylmagnesium bromide in diethyl ether in order to study the low temperature nmr spectrum of this compound for structure elucidation purposes. However, a solid was obtained from this reaction which had a Br:Mg:Al ratio of 1.2:1.0:0.80. The infrared spectrum of the solid exhibited bands at 1680 (broad) and 710 cm^{-1} (broad) and also bands corresponding to magnesium hydride. The analysis of the solution obtained from this reaction by filtration of the solid gave upon elemental analysis a Mg:Al ratio of 1.0:2.12. The conclusion is that $HMgAlH_3(CH_3)$ is unstable and disproportionates to MgH_2 and $Mg(AlH_3CH_3)_2$ at room temperature.

$$NaAlH_4 + CH_3MgBr \rightarrow NaBr + HMgAlH_3CH_3 \quad (20)$$

$$2\ HMgAlH_3CH_3 \rightarrow MgH_2 + Mg(AlH_3CH_3)_2 \quad (21)$$

Sodium aluminum hydride was allowed to react with s-butylmagnesium chloride in diethyl ether in a 1:1 mole ratio. The solution obtained by filtration gave upon elemental analysis a Mg:Al ratio of 1.0:1.67. The infrared spectrum of the filtrate showed broad bands at 1780 and 720 cm^{-1}.

The solid resulting from this filtration gave a Mg:Al:Cl ratio of 1.0:0.3:2.0. This solid respresented 50.8% of the initial amount of magnesium. The infrared spectrum of the solid showed bands corresponding to magnesium hydride but no bands were observed characteristic of the Al-H stretching region. Similar results were obtained in the reaction of lithium aluminum hydride with sec-butylmagnesium chloride. The conclusion is similar to that arrived at earlier in the reaction of $NaAlH_4$ with methylmagnesium bromide, that is, the initial product $[HMgAlH_3(s\text{-}C_4H_9)]$ disproportionates to MgH_2 and $Mg[AlH_3(s\text{-}C_4H_9)]_2$ under the conditions of the reaction.

$$NaAlH_4 + s\text{-}C_4H_9MgCl \rightarrow NaCl + HMgAlH_3(s\text{-}C_4H_9) \quad (22)$$

$$2\ HMgAlH_3(s\text{-}C_4H_9) \rightarrow MgH_2 + Mg[AlH_3(s\text{-}C_4H_9)]_2 \quad (23)$$

In an effort to prepare sec-butylmagnesium aluminum hydride by an alternate route, sec-butyllithium was allowed to react with iodomagnesium aluminum hydride in a 1:1 mole ratio in cyclohexane at 0°. After the reaction mixture was filtered, analysis of the filtrate showed a Mg:Al ratio of 1.0:1.8. The infrared spectrum of the solid corresponded to magnesium hydride and showed no bands due to the Al-H stretching mode. The X-ray powder pattern showed the solid to contain lithium iodide. The conclusion is that a metathetical exchange reaction occurs producing LiI and $s\text{-}C_4H_9MgAlH_4$ which then rearrange to $HMgAlH_3(s\text{-}C_4H_9)$ which subsequently disproportionates to MgH_2 and $Mg[AlH_3(s\text{-}C_4H_9)]_2$.

$$s\text{-}C_4H_9Li + IMgAlH_4 \rightarrow LiI + HMgAlH_3(s\text{-}C_4H_9) \quad (24)$$

$$2\ HMgAlH_3(s\text{-}C_4H_9) \rightarrow MgH_2 + Mg[AlH_3(s\text{-}C_4H_9)]_2 \quad (25)$$

When $LiAlH_4$ was allowed to react with phenylmagnesium bromide at a mole ratio of 1:6 the physical observations corresponded to those reported by Rice,[2] that is, a solid was formed in the reaction and a brown lower layer appeared. The solid was dissolved in benzene and recrystallized by addition of diethyl ether. Analysis of this solid gave a Br:Al:Mg:H ratio of 0.41:0.27:1.79:1.0. The weight percent found for Mg, 10.24 and H, 0.235 are not far from those reported by Rice (Mg, 9.62 and H, 0.195). Rice attributes this analysis to the formation of $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3[O(C_2H_5)_2]$ (Mg, 9.62; H, 0.198). The amount of magnesium in the solid corresponded to 16% of the total magnesium. The infrared spectrum of the solid obtained after recrystallization had infrared absorption bands at approximately 700 cm^{-1} characteristic of monosubstituted phenyl groups. There were no bands between 500-600 cm^{-1}, however, there was a band at 480 cm^{-1} which could be attributed to Mg-C stretching. No evidence of $LiAlBr_4$ was found, however, analysis of the lower layer produced in the reaction after extraction with benzene did give an Al:Br ratio of 1.0:1.0 with magnesium present in excess indicating the possibility of $BrMgAl(C_6H_5)_4$ as observed in the 1:6 case for the reaction of $LiAlH_4$ with $n\text{-}C_4H_9MgBr$. The $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3[O(C_2H_5)_2]$ reported by Rice could be envisioned as resulting from the following sequence of reactions.

$$2\ C_6H_5MgBr \rightleftharpoons (C_6H_5)_2Mg + MgBr_2 \qquad (26)$$

$$4(C_6H_5)_2Mg + LiAlH_4 \rightarrow 4(C_6H_5MgH) + LiAl(C_6H_5)_4 \qquad (27)$$

$$(C_6H_5)_2Mg + C_6H_5MgH \rightarrow (C_6H_5)_2Mg \cdot C_6H_5MgH \qquad (28)$$

The Schlenk equilibrium for C_6H_5MgBr in ether shows an approximately statistical distribution between the C_6H_5MgBr and $(C_6H_5)_2Mg$ and $MgBr_2$ (eq. 26). When $LiAlH_4$ is added to phenylmagnesium bromide, it is reasonable that reaction takes place between $LiAlH_4$ and $(C_6H_5)_2Mg$ to form C_6H_5MgH which is then stabilized by reaction with $(C_6H_5)_2Mg$ to form a complex. We have recently prepared similar complexes ($RMgH \cdot R_2Mg$) where R=CH_3, n-C_4H_9 and C_6H_5 by the hydrogenolysis of unsymmetrical dialkylmagnesium compounds.[8]

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(8) Unpublished results.

$$2(RMgR') \xrightarrow[\Delta]{H_2} RMgH \cdot RMgR' + R'H \qquad (29)$$

The formation of $BrMgAl(C_6H_5)_4$ in the reaction of $LiAlH_4$ with $(C_6H_5)_2Mg$ in 1:6 ratio can be explained by the following sequence of reactions.

$$LiAlH_4 + MgBr_2 \rightarrow BrMgAlH_4 + LiBr \qquad (30)$$

$$BrMgAlH_4 + 4(C_6H_5)_2Mg \rightarrow BrMgAl(C_6H_5)_4 + 4(HMgC_6H_5) \qquad (31)$$

When $LiAlH_4$ was allowed to react with C_6H_5MgBr in a 1:1 ratio the lower layer observed initially disappeared and the amount of solid increased relative to the amount observed when the reaction was carried out in 1:6 ratio. When the solid was filtered, elemental analysis showed a Mg:H ratio of 1.0:1.94. This analysis as well as infrared and X-ray powder pattern analysis shows the solid to be MgH_2. The amount of magnesium in the solid accounts for 48.41 percent of the original magnesium

Elemental analysis of the filtrate showed a Br:Mg:Al ratio of 2.1:1.0:1.91. The infrared spectrum of the solution showed a broad band at 1750 cm^{-1} and also bands at 1245, 895, 770 and 705 cm^{-1}. These results are analogous to those observed in the reaction of $LiAlH_4$ with s-butylmagnesium bromide indicating that $HMgAlH_3C_6H_5$ disproportionates to MgH_2 and $Mg[AlH_3(C_6H_5)]_2$.

Reactions of Grignard Compounds with Excess $LiAlH_4$. - Reactions of $LiAlH_4$ with Grignard reagents in ether at 1.0:1.0 stoichiometry or excess Grignard reagent have just been discussed. The importance of studying reactions in which $LiAlH_4$ is in excess lies in the realization that $HMgAlH_3R$ compounds might be converted to $HMgAlH_4$ according to eq. 32.

$$HMgAlH_3R + LiAlH_4(\text{excess}) \rightleftharpoons HMgAlH_4 + LiAlH_3R \qquad (32)$$

In this connection $LiAlH_4$ was allowed to react with $HMgAlH_3(n\text{-}C_4H_9)$ in 3:1 ratio. A trace amount of solid was obtained which gave a Mg:Al:H ratio of 0.0:1.0:2.8. After filtration the solvent was removed from the filtrate and the X-ray powder pattern of the resulting solid showed only lines corresponding to the starting materials, $LiAlH_4$ and $HMgAlH_3(n\text{-}C_4H_9)$.

When $n\text{-}C_4H_9MgCl$ was added to $LiAlH_4$ in ether at a ratio of 1:4, a solid was obtained which after filtration was shown by elemental analysis and X-ray powder pattern to be LiCl. The solvent was then removed from the filtrate. The X-ray powder pattern of the resulting solid corresponded to a physical mixture of $LiAlH_4$ and $HMgAlH_3n\text{-}C_4H_9$. The results of these experiments indicate that $HMgAlH_3n\text{-}C_4H_9$ does not react with $LiAlH_4$ according to eq. 32.

When sodium aluminum hydride was allowed to react with $n\text{-}C_4H_9MgBr$ in THF the products were somewhat different compared to the same reaction

using $LiAlH_4$ due to the insolubility of the NaBr by-product. At 1:1 ratio, a solid formed which had a Mg:Al ratio of 1.0:1.1. This solid accounts for about 10 percent of the original magnesium. The infrared spectrum of the solid corresponded to $Mg(AlH_4)_2 \cdot 4THF$. The X-ray powder pattern of the solid shows lines corresponding to a physical mixture of NaBr and $Mg(AlH_4)_2 \cdot 4THF$. The elemental analysis of the solution gave a Br:Mg:Al ratio of 0.0:1.04:1.0. The infrared spectrum of the solution corresponds to $HMgAlH_3n\text{-}C_4H_9$. The $Mg(AlH_4)_2$ noted above could result from the reaction of $NaAlH_4$ with $MgBr_2$ present in the Schlenk equilibrium.

Lithium aluminum hydride was allowed to react with n-butylmagnesium bromide in 1:1 ratio in THF. No precipitate was produced during the reaction. The infrared spectrum of the solution showed bands at 1700, 790 and 755 cm^{-1}. These bands correspond to those observed previously for $HMgAlH_3(n\text{-}C_4H_9)$ formed in diethyl ether and redissolved in THF.

In addition to studying the reaction of $LiAlH_4$ with RMgX compounds we also studied the reactions of $LiAlH_4$ with yMgX compounds where y = OR and NR_2. The objective of this work was to prepare $ROMgAlH_4$ and $R_2NMgAlH_4$ compounds which then might be hydrogenolyzed to $HMgAlH_4$. This objective was based on our earlier observation that R_2NMgH compounds can be hydrogenolyzed to R_2NH and MgH_2[9] and, therefore, $R_2NMgAlH_4$ might hydrogenolyze to R_2NH and $HMgAlH_4$.

$$R_2NMgH \xrightarrow{H_2} R_2NH + MgH_2 \qquad (33)$$

(9) R. G. Beach and E. C. Ashby, Inorg. Chem., 10, 906 (1971).

In the reaction of lithium aluminum hydride with isopropoxymagnesium bromide in a 1:1 mole ratio, results similar to those obtained in the Grignard case were observed. Filtration of the reaction mixture yields a solution whose elemental analysis shows a Mg:Al:Br ratio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained by filtration corresponds to magnesium hydride and shows no bands characteristic of the Al-H stretching modes. These results indicate that the $i\text{-}C_3H_7OMgAlH_4$ initially formed rearranges to $HMgAlH_3(Oi\text{-}C_3H_7)$ and then disproportionates to MgH_2 and $Mg[AlH_3(Oi\text{-}C_3H_7)]_2$.

$$C_2H_5MgBr + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OMgBr + C_2H_6 \quad (34)$$

$$i\text{-}C_3H_7OMgBr + LiAlH_4 \rightarrow i\text{-}C_3H_7OMgAlH_4 + LiBr \quad (35)$$

$$i\text{-}C_3H_7OMgAlH_4 \rightarrow HMgAlH_3(Oi\text{-}C_3H_7) \quad (36)$$

$$2[HMgAlH_3(Oi\text{-}C_3H_7)] \rightarrow MgH_2 + Mg[AlH_3(Oi\text{-}C_3H_7)]_2 \quad (37)$$

Dibutylaminomagnesium aluminum hydride was prepared by the reaction of lithium aluminum hydride and di-n-butylaminomagnesium chloride in a 1:1 mole ratio. The elemental analysis of the solution obtained from filtration of the reaction mixture gave a Mg:Al:Cl ratio of 1.01:1.00:0.0. The infrared spectrum of the solution showed bands at 1830 (sharp), 870 cm^{-1} with a broad band at 740 cm^{-1}. The compound $(n\text{-}C_4H_9)_2NMgAlH_4$ is also soluble in benzene as the diethyl etherate.

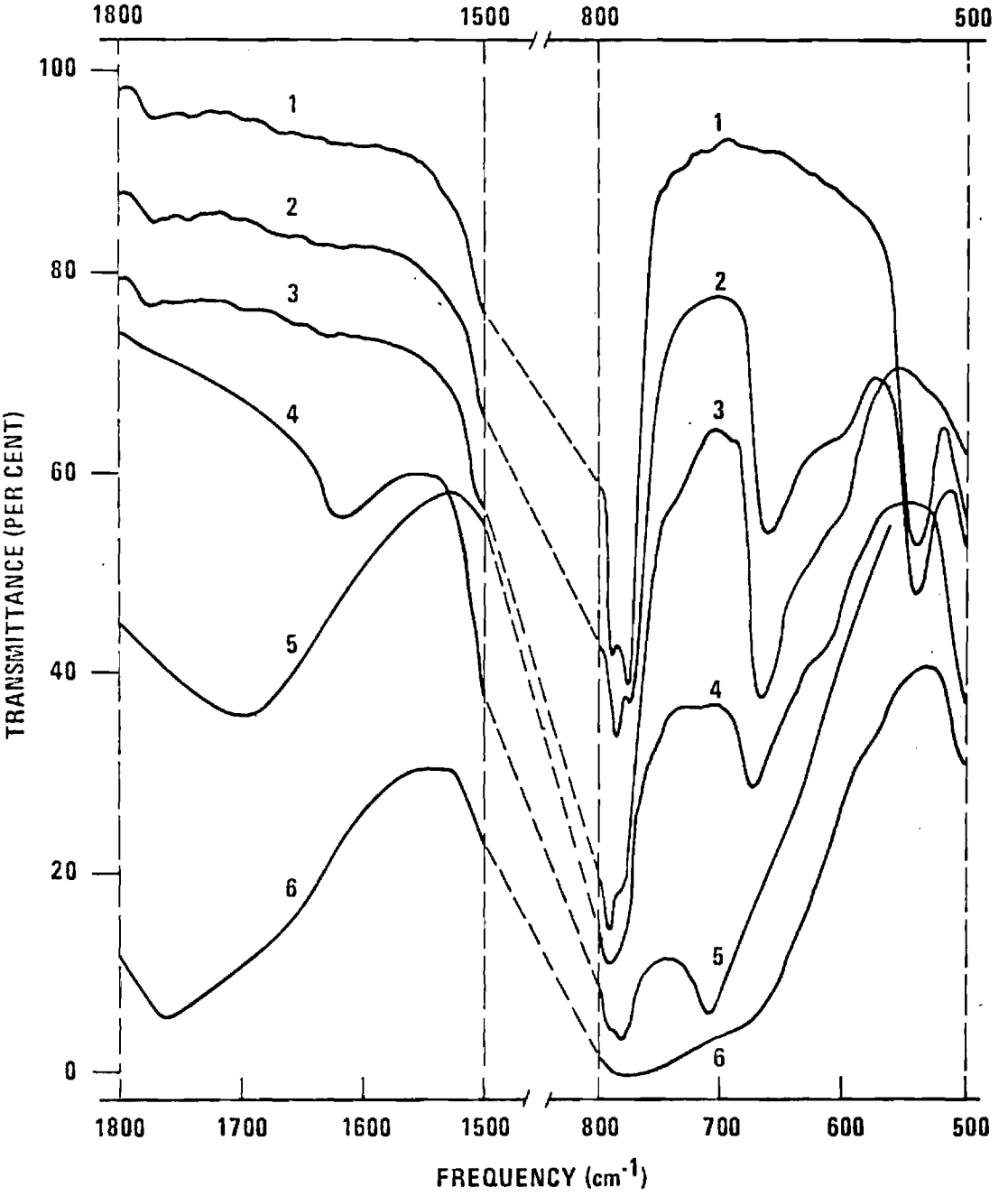
$$(n\text{-}C_4H_9)_2NH + C_2H_5MgCl \rightarrow (n\text{-}C_4H_9)_2NMgCl + C_2H_6 \quad (38)$$

$$LiAlH_4 + ClMgN(n\text{-}C_4H_9)_2 \rightarrow LiCl + (n\text{-}C_4H_9)_2NMgAlH_4 \quad (39)$$

To summarize, the reaction of $LiAlH_4$ and $NaAlH_4$ with Grignard reagents has been shown to proceed in a stepwise fashion according to equations 5-11. Various intermediates involved in the stepwise process, such as $BrMgAlR_4$ and $BrMg_2AlH_4R_2$, have been isolated and characterized. The stability of the $HMgAlH_3R$ compounds produced by the reaction of $LiAlH_4$ with RMgX in 1:1 ratio was found to be dependent on the nature of the alkyl group. When R=n-C_4H_9, C_2H_5, and C_6H_5 the $HMgAlH_3R$ compounds are stable. When R=CH_3 and s-C_4H_9, the compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether except when the alkali metal by-product is insoluble in THF. In this case $Mg(AlH_4)_2$ was formed in approximately 10% yield whereas the remainder of the product in solution was found to be $HMgAlH_3R$.

Acknowledgement: We are indebted to the Office of Naval Research under Contract No. N000 14-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

Figure 1. Infrared examination of the soluble reaction product in the reaction of $LiAlH_4$ with n-butylmagnesium bromide in diethyl ether. Mole ratio of $LiAlH_4$:n-C_4H_9MgBr (1) 0:1.0; (2) 0.16:1.0; (3) 0.25:1.0; (4) 0.33:1.0; (5) 0.5:1.0; (6) 1.0:1.0.


1800
1500
800
500
100
80
60
40
20
0
TRANSMITTANCE (PER CENT)
1
2
3
4
5
6
1800
1700
1600
1500
800
700
600
500
FREQUENCY (cm-1)

APPENDIX

[Reprinted from Inorganic Chemistry, 10, 893 (1971).]

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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Aminoalanes. Direct Synthesis from Aluminum, Hydrogen, and Secondary Amines. Structure and Stability Elucidation by Nuclear Magnetic Resonance, Infrared Spectra, and Differential Thermal and Thermal Gravimetric Analysis

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Received August 11, 1970

Detailed studies of the synthesis of aminoalanes by the direct reaction of aluminum, hydrogen, and secondary amines are reported. Tris- and bis(diethylamino)alanes are prepared in high yield depending on the reaction conditions and on the initial amine to aluminum molar ratio. Reaction of aluminum and diethylamine in molar ratios ranging from 1:1 to 2:1 at 150° afforded high yields of bis(diethylamino)alane ($HAl[N(C_2H_5)_2]_2$). Only low yields of diethylaminoalane ($H_2AlN(C_2H_5)_2$) were formed in admixture with bis(diethylamino)alane under conditions most suitable for forming only diethylaminoalane. The reactions of aluminum and hydrogen with dimethyl-, diisopropyl-, and diphenylamine, pyrrolidine, and piperidine were also carried out. As in the case with diethylamine, predominant formation of the bis(dialkylamino)alane was observed with dimethylamine, piperidine, and pyrrolidine. *No reactions* were observed with diisopropyl- and diphenylamine. Predominant formation of bis(dialkylamino)alanes in preference to dialkylaminoalanes is attributed to the greater thermodynamic stability of the former compounds. Verification of this point was accomplished by dta–tga and solution pyrolysis studies. Proton magnetic resonance and infrared spectral measurements of the aminoalanes are reported and interpreted to yield valuable analytical and structural information.

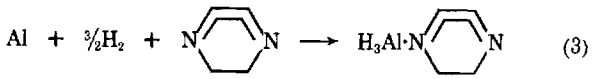
Introduction

Aminoalanes ($H_{3-n}Al(NR_2)_n$, n = 1–3) have been used as polymerization catalysts,[1] reducing agents,[2] and synthetic intermediates;[3] however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoalanes have been prepared by the reactions of (1) alane[4] or trimethylamine–alane[5] with secondary amines (eq 1) and (2) lithium aluminum hydride and dialkylammonium chlorides[6] (eq 2).

$$AlH_3 + nHNR_2 \longrightarrow nH_2 + H_{3-n}Al(NR_2)_n \quad (n = 1\text{–}3) \quad (1)$$

$$LiAlH_4 + R_2NH_2Cl \longrightarrow LiCl + 2H_2 + H_2AlNR_2 \quad (2)$$

In 1964 we reported the direct synthesis of an amine–alane by the reaction of triethylenediamine with aluminum and hydrogen in tetrahydrofuran under mild conditions[7] (eq 3). The reaction of a secondary amine,



$$Al + \tfrac{3}{2}H_2 + \text{triethylenediamine} \longrightarrow H_3Al\cdot\text{triethylenediamine} \quad (3)$$

aluminum, and hydrogen was predicted to follow an analogous path involving intermediate formation of AlH_3 followed by complexation of the secondary amine to form AlH_3NR_2H. Since dialkylamine–alanes are unstable and lose hydrogen well below room temperature,[3] the dialkylaminoalane (H_2AlNR_2) should be the first product capable of being isolated. In the presence of additional secondary amine, the dialkylaminoalane should react further to form the bis(dialkylamino)alane [$HAl(NR_2)_2$] and in the presence of additional dialkylamine, the tris(dialkylamino)alane, [$HAl(NR_2)_3$], according to eq 4. We have now made a detailed study[8] of the reaction of aluminum, hydrogen, and secondary amines as a route to aminoalanes and wish to report the results herein. This reaction represents such a convenient and economic route to aminoalanes that further investigation of new uses of aminoalanes should be encouraged. We are at present carrying out a detailed evaluation of this class of compounds as selective reducing agents in organic chemistry.

$$Al + H_2 \longrightarrow AlH_3 \xrightarrow{R_2NH} AlH_3\cdot NR_2H \xrightarrow[-H_2]{} H_2AlNR_2 \xrightarrow[-H_2]{R_2NH} HAl(NR_2)_2 \xrightarrow[-H_2]{R_2NH} Al(NR_2)_3 \quad (4)$$

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of standard bench-top techniques[9] or employment of a drybox equipped with a recirculating atmosphere purification system for removal of oxygen and moisture.[10] Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained using neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using the solvent signal (benzene) as internal standard.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from $NaAlH_4$ prior to use. Dimethylamine (anhydrous) was purchased from the Matheson Corp. and passed through a KOH drying tube prior to use. Diethyl-, diisopropyl-, and diphenylamine, piperidine, and pyrrolidine were purchased from Eastman Chemical Co. The liquid dialkylamines were either distilled from anhydrous KOH or distilled onto active molecular sieve, Type 4-A, prior to use. Diphenylamine was used without further purification. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. Aluminum was "activated" prior to use by the method described by Ziegler.[11] Ultra pure hydrogen (99.9995%) was obtained from the Matheson Corp. and used without further purification.

Analyses.—Aminoalanes are readily hydrolyzed by water and dilute acids. Analyses were performed by hydrolyzing a tared sample with a water–acid mixture and determination of the hydrogen content by gas evolution analysis. Aluminum in the same sample was determined by EDTA titration. Amines were

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(4) E. Wiberg and A. May, *Z. Naturforsch. B*, **10**, 234 (1955).
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(9) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.
(10) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).
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determined by potentiometric titration of the solution obtained on hydrolysis of a tared sample after removal of the $Al(OH)_3$.

Synthesis.—Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave (Autoclave Engineers, Inc.). The chamber was usually charged in the drybox. The contents were then heated under hydrogen for a predetermined period. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum in the drybox. The solvent was then removed from the clear filtrate under vacuum and the product was analyzed as the neat material. Reaction conditions and results for the reactions studied are reported in Table II and elemental analyses of the reaction products are reported in Table I. The analyses were performed

TABLE I
ELEMENTAL ANALYSIS OF AMINOALANES

		Analyses, %					
		Al		Amine		Hydridic hydrogen	
Compd	Mol wt	Calcd	Found	Calcd	Found	Calcd	Found
$Al[N(CH_3)_2]_3$	159	17.0	16.8	...	...	...	...
$HAl[N(CH_3)_2]_2$	116	23.3	24.6	...	...	0.863	0.93
$Al[N(C_2H_5)_2]_3$	243	11.1	12.8	88.9	87.6	...	...
$HAl[N(C_2H_5)_2]_2$	172	15.7	16.0	83.7	84.4	0.582	0.612
$H_2AlN(C_2H_5)_2$	101	26.7	26.1	71.3	71.9	1.98	1.96
$HAl(N\square)_2$	196	13.8	13.8	85.7	85.6	0.510	0.53
$H_2AlN\square$	113	23.9	24.1	74.3	74.1	1.77	1.83
$HAl(N\square)_2$	168	16.1	15.8	83.3	82.8	0.595	0.599
$H_2AlN\square$	99	27.3	27.2	70.7	68.9	2.01	1.87
$HAl[N(i\text{-}C_3H_7)_2]_2$	228	11.8	12.2	87.7	86.7	0.439	0.441
$H_2AlN(i\text{-}C_3H_7)_2$	129	20.9	19.8	77.5	77.3	1.55	1.49

on the unpurified reaction product. Further establishment of the nature of the reaction products was made by infrared and nmr comparisons with an authentic sample of the product synthesized by unequivocal means. In every case the spectra were identical.

Reaction of Aluminum, Hydrogen, and $Al[N(CH_3)_2]_3$.—Tris(dimethylamino)alane (0.10 mol from the reaction of 0.1 mol of trimethylamine–alane and excess dimethylamine), aluminum, (5 g or 0.15 mol), and benzene (100 ml) were heated at 120° under 4000 psig of hydrogen for 12 hr. The resulting mixture was filtered in the drybox yielding a clear filtrate. The filtrate was diluted to a known volume (120 ml) with benzene and analyzed for hydridic hydrogen and aluminum. *Anal.* Found: H, 1.11 *M*; Al, 1.19 *M*. The hydrogen:aluminum ratio was 0.93:1.00, indicating formation of bis(dimethylamino)alane. The proton nmr spectrum of the benzene solution matched exactly that of authentic bis(dimethylamino)alane. These analytical data indicate that the yield of bis(dimethylamino)alane is 0.145 mol.

Unequivocal Synthesis of Aminoalanes.—Dialkylamino- and bis(dialkylamino)alanes were prepared by the reaction of trimethylamine–alane and 1 or 2 equiv of the appropriate secondary amine, in benzene solution.[5] The solutions were usually stirred for 2 hr after initial mixing of the reagents. Products were isolated by removing the solvent under vacuum. These compounds were analyzed for hydrogen and aluminum and the experimental values were found to agree with the calculated values to within 5% in all cases. The following compounds were synthesized: $H_2AlN(C_2H_5)_2$, $HAl(N(C_2H_5)_2)_2$, $H_2AlNC_5H_{10}$, $HAl(NC_5H_{10})_2$, $H_2AlNC_4H_8$, $HAl(NC_4H_8)_2$, $H_2AlN(i\text{-}C_3H_7)_2$.

Forcing conditions and additional time were required for the preparation of bis(diisopropylamino)alane. The hydrogen and aluminum ratio of a 2:1 *M* mixture of diisopropylamine and trimethylamine–alane in benzene was found to be 1.8:1.0 after simple stirring at room temperature for 2 hr. This ratio was reduced to 1.5:1.0 and 1.05:1.00 after heating at reflux for 24 and 48 hr, respectively.

Tris(dimethylamino)alane was prepared by the reaction of trimethylamine–alane in benzene solution with excess dimethylamine. (Dimethylamine was allowed to bubble through the stirred alane solution at room temperature until liberation of hydrogen at the gas dispersion frit was observed to cease.) Attempts to prepare tris(diethylamino)alane by the reaction of equimolar mixtures of bis(diethylamino)alane and diethylamine by refluxing these reagents in benzene solution for as long as 12 hr failed as evidenced by the fact that hydridic hydrogen was found in solution. The reaction could be forced to completion by the reaction of bis(diethylamino)alane in diethylamine for 12 hr at reflux temperature. Tris(piperidino)alane was prepared in an analogous way by the reaction of trimethylamine–alane and ~10-fold excess piperidine in benzene.

Pyrolysis Studies of Aminoalane Compounds. A. Pyrolysis of $H_2AlNC_5H_{10}$ in Refluxing Toluene.—Piperidinoalane (1.08 g or 9.6 mmol) was dissolved in 30 ml of toluene and heated at reflux with stirring. Aliquot samples (2.0 ml) were withdrawn at appropriate intervals with a syringe. Toluene was removed under vacuum and the solid thus obtained was dissolved in 0.5 ml of benzene (toluene was removed since the methyl resonance of toluene was found to interfere in the proton magnetic resonance study) and proton magnetic resonance spectra of the samples were recorded. These spectral data are shown in Figure 1.

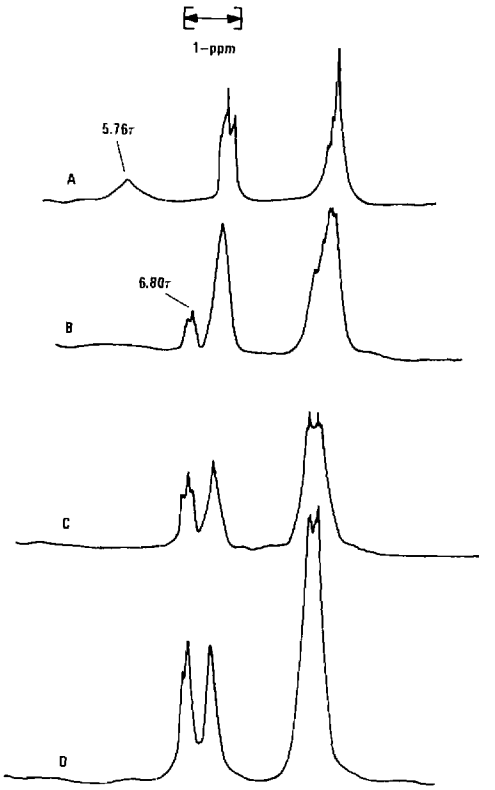


Figure 1.—Proton magnetic resonance spectral study of the pyrolysis of $H_2AlNC_5H_{10}$ in boiling toluene. Spectra were recorded in benzene solution: A, $t = 0$ spectrum of piperidinoalane; B, spectrum obtained after heating for 2.5 days; C, after heating for 6.5 days; D, after heating for 8.5 days.

The spectral changes were complete after heating for 8.5 days. After this period of heating the aluminum to hydrogen ratio was found to be 1.0:1.1. A dark gray, metallic precipitate (presumed to be aluminum) formed during this period.

B. Dta–Tga Analysis of Aminoalanes.—The thermal behavior of H_2AlNR_2 and $HAl(NR_2)_2$ compounds (NR_2 = $N(C_2H_5)_2$, NC_5H_{10}, NC_4H_8) was studied by simultaneous differential thermal and thermal gravimetric analyses of these compounds using Mettler Thermoanalyzer II instrumentation. Samples were loaded into tared platinum crucibles in the drybox and subjected to dta–tga analysis under a steady flow of argon. Representative thermal data obtained for analysis of $H_2AlNC_5H_{10}$ and $HAl(NC_5H_{10})_2$ are shown in Figure 2. The bulk of the thermal properties are summarized in Table IV.

C. Pyrolysis of H_2AlNR_2 Compounds in Evacuated, Sealed Tubes.—Piperidinoalane (0.1247 g or 1.107 mmol) was sealed in an evacuated break-seal bulb of approximately 20-ml volume. The entire assembly was submerged into a 200° oil bath for 15 min. After cooling, the tube was attached to a vacuum manifold by means of an "O" ring gasket seal and hydrogen (0.755

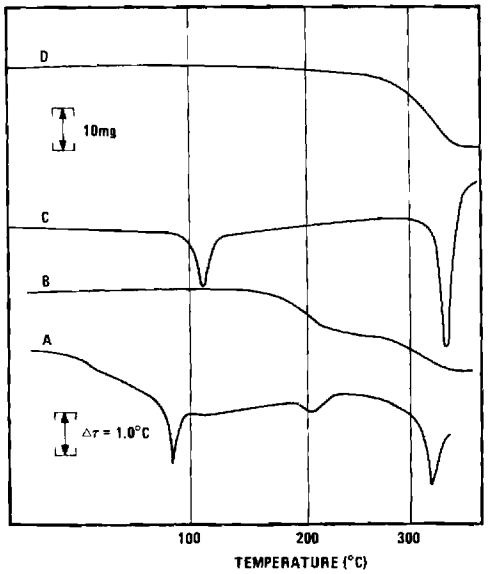


Figure 2.—Dta-tga traces of $H_2AlNC_5H_{10}$ and $HAl(NC_5H_{10})_2$. A and B are dta and tga traces for $H_2AlNC_5H_{10}$, respectively (sample size 53.0 mg); C and D are dta and tga traces for $HAl(NC_5H_{10})_2$, respectively (53.7 mg).

mmol) was determined by gas evolution analysis after opening the break-seal with a magnet. Residual solid was dissolved in benzene and the proton magnetic resonance spectrum of the resulting solution was recorded. This spectrum was found to be identical with that of authentic bis(piperidino)alane (Figure 3).

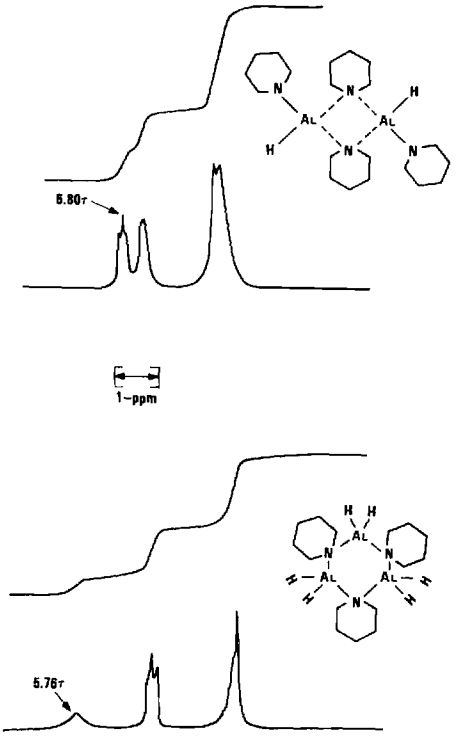


Figure 3.—Representative proton magnetic resonance spectra of mono- and bis(piperidino)alane in benzene solution.

Hydrogen (1.1 mmol) was isolated in an analogous experiment by heating diethylaminoalane (0.1531 g or 1.516 mmol) at 180° for 15 min. A dark gray, metallic precipitate (assumed to be aluminum) formed during each of these pyrolyses.

Results and Discussion

Direct Preparation of Aminoalanes.—The reaction of aluminum and hydrogen with secondary amines was studied in most detail with diethylamine and the

TABLE II
REACTIONS OF ALUMINUM, HYDROGEN, AND DIETHYLAMINE IN BENZENE SOLVENT[a]

$$Al + {}^3/_2H_2 + nR_2NH \xrightarrow{\Delta,P} H_{3-n}Al(NR_2)_n + nH_2$$

Reaction no.	Al:amine molar ratio	Time, hr	Products	Yield, %
1	1:1	3	$HAl(NR_2)_2$	92
2	Excess Al	3	$HAl(NR_2)_2$	98
3	Excess Al	7	$HAl(NR_2)_2$	86
			H_2AlNR_2	9
4	Excess Al	16	$HAl(NR_2)_2$	91
			H_2AlNR_2	4
5	Excess Al	28	$HAl(NR_2)_2$	90
			$H_2Al(NR_2)$	3
6	Excess Al[b]	24	$HAl(NR_2)_2$	78
			H_2AlNR_2	15
7	1:4	3	$HAl(NR_2)_2$	5
			$Al(NR_2)_3$	88
8	Excess amine (amine solvent)	4	$Al(NR_2)_3$	91

[a] R = C_2H_5; n = 1–3; temperature 150°; pressure 3000–4000 psi. [b] Reaction temperature 65°.

results are summarized in Table II. Bis(diethylamino)alane was the only compound formed when equivalent quantities of aluminum and diethylamine were heated under hydrogen pressure for 3 hr (reaction 1, Table II). The product from this reaction was isolated and analyzed successfully for $HAl(N(C_2H_5)_2)_2$. The proton magnetic resonance spectrum (in benzene) and infrared spectrum were identical with spectra of the analogous product prepared by unequivocal synthesis. Although bis(diethylamino)alane was formed

$$2H_2 + 2Al + 4HN(C_2H_5)_2 \longrightarrow 2HAl(N(C_2H_5)_2)_2 + 3H_2 \quad (5)$$

in high yield, efforts to prepare diethylaminoalane by increasing the aluminum to diethylamine molar ratio (reaction 2) and extending reaction times (reactions 3–5) were largely unsuccessful. The hydrogen:aluminum ratio in the products obtained in these reactions was always slightly higher than unity, indicating a low yield of the diethylaminoalane (yields ranged from 3 to 9%). These results indicate that the reaction of aluminum, hydrogen, and bis(diethylamino)alane to form diethylaminoalane does not occur to any appreciable extent at 150°. Reaction at 65° produced a material

$$2Al + 3H_2 + 2HAl(N(C_2H_5)_2)_2 \xrightarrow{150°} 4H_2AlN(C_2H_5)_2 \quad (6)$$

which revealed a hydrogen to aluminum ratio of 1.19:1.0 indicating a ratio of bis(diethylamino)alane to diethylaminoalane of 78:15. Infrared analysis also revealed the product to be a mixture of the mono- and bis(amino)alane. On the other hand tris(dimethylamino)alane reacted readily and cleanly according to the equation

$$Al[N(CH_3)_2]_3 + {}^1/_2Al + {}^3/_4H_2 \xrightarrow{\text{benzene}} {}^3/_2HAl[N(CH_3)_2]_2 \quad (7)$$

These data suggest that bis(diethylamino)alane is the preferred product in this reaction and is thermodynamically more stable than diethylaminoalane and thus the former compound is produced in high yield under conditions predicted to form either. This was verified by pyrolysis studies of diethylaminoalane (*vide infra*).

It is interesting to note that even at an aluminum:amine ratio of 1:4 some (5%) bis(diethylamino)alane remained in admixture with tris(diethylamino)alane; however, the latter compound was produced in high yield (91%) when diethylamine was used as the sol-

vent. These results suggest that forcing conditions are required to prepare tris(dialkylamino)alanes, due presumably to steric crowding in the product. This conclusion was substantiated by our attempts to prepare tris(diethylamino)alane by the reaction of equivalent molar quantities of bis(diethylamino)alane and diethylamine in benzene solution. The replacement of all hydridic hydrogen was incomplete even after refluxing for 12 hr. The reaction could only be forced to completion by using diethylamine as the solvent and refluxing for 12 hr.

The scope of the reaction of aluminum, hydrogen, and diethylamine was investigated using other secondary amines. The amines were chosen based on their relative base strengths as determined by both electronic and steric factors. These included dimethyl-, diisopropyl-, and diphenylamine, piperidine, and pyrrolidine. The results of these experiments are summarized in Table III.

TABLE III
REACTIONS OF ALUMINUM, HYDROGEN, AND SELECTED DIALKYLAMINES IN BENZENE SOLVENT[a]

$$Al + {}^3/_2H_2 + nR_2NH \xrightarrow{\Delta,P} H_{3-n}Al(NR_2)_n + nH_2$$

Reaction no.	Amine	Time, hr	Temp, °C	Products	Yield, %
1	$HN(CH_3)_2$	4	150	$HAl(N(CH_3)_2)_2$	91
2	$HN(CH_3)_2$	20	110	$HAl(N(CH_3)_2)_2$	72
				$H_2AlN(CH_3)_2$	18
3	$HN(CH_3)_2$	20	60	No reaction	
4	Piperidine	5	180	$H_2AlNC_5H_{10}$	0.9
				$HAl(NC_5H_{10})_2$	83
5	Piperidine	20	110	$H_2AlNC_5H_{10}$	3.5
				$HAl(NC_5H_{10})_2$	89
6	Pyrrolidine	12	150	$HAl(NC_4H_8)_2$	88
7	$HN(i\text{-}C_3H_7)_2$	4	110	No reaction	
8	$HN(C_6H_5)_2$	4	140	No reaction	

[a] Pressure 3000–4000 psi; aluminum:amine ratio 1.5:1.

As was the case with diethylamine, predominant formation of the bis(dialkylamino)alane was observed by reaction of aluminum (in excess) with dimethylamine (reaction 1), piperidine (reaction 4), and pyrrolidine (reaction 6). Low yields of the corresponding dialkylaminoalane were observed when these reactions were run at lower temperature (reactions 2, 5).

No reaction was observed when the secondary amine was diisopropylamine or diphenylamine, indicating that the base strength of the secondary amine is an important factor in the direct preparation reaction. It is believed that AlH_3 is generated in this reaction but that further reaction with these secondary amines is not sufficiently fast nor is the ΔH_f of the amine–alane sufficiently large to compete with thermal autodecomposition of the AlH_3.[12] This explanation is supported by our observations concerning the relative reactivities of a series of secondary amines with trimethylamine–alane in benzene. This route to the bis(dialkylamine)–alanes proceeded rapidly and cleanly in ~2 hr by simple stirring of the amine–alane with diethylamine, piperidine, and pyrrolidine, while forcing conditions and a reaction time of ~48 hr (see Experimental Section) were required for the preparation of bis(diisopropylamino)alane.

Thermal Properties of Aminoalanes.—The direct-synthesis study suggests that bis(dialkylamino)alanes are thermodynamically more stable than the corresponding dialkylaminoalanes and thus the former compounds are formed preferentially at the reaction temperatures employed. Unfortunately little information is available concerning the thermal stabilities of aminoalanes. Wiberg[4] reported that dialkylaminoalanes decompose upon heating above their melting points with precipitation of dark flakes. No details concerning the pyrolysis were reported and the exact products of decomposition are unknown. Nöth[8] suggested that the expected decomposition products might include aluminum, hydrogen, $HAl(NR_2)_2$, or $Al(NR_2)_3$, etc. On the other hand, it is known that the corresponding bis(dialkylamino)alanes are quite stable thermally. Thus, it has been reported that bis(dimethylamino)- and bis(diisopropylamino)alane can be heated under normal pressure with refluxing, without decomposition.[3]

The thermal decomposition of dialkylaminoalanes has been studied by quantitative determination of pyrolysis products under exact pyrolysis conditions. The pyrolysis of piperidinoalane was studied most thoroughly since this compound can be separated easily from possible decomposition products by sublimation. In addition, spectroscopic properties of this compound and predicted decomposition products are unique and can in fact be used to follow the pyrolysis reaction. It was intended that results obtained from a study of this system could be extended to describe pyrolysis of other dialkylaminoalanes.

In one pyrolysis experiment, piperidinoalane was heated at reflux in toluene. Aliquot samples were withdrawn at appropriate intervals, the solvent was removed under vacuum and replaced by benzene, and the proton magnetic resonance spectrum of the benzene solution was recorded. These data are summarized in Figure 1. The initial ($t = 0$) spectrum of piperidinoalane changed considerably by heating at 110° for 2.5 days. The hydride signal of this compound at τ 5.76 is broadened and a new signal (triplet at τ 6.80) is present. The pyrolysis was continued by refluxing for longer periods. After 6.5 days the signal due the hydridic proton was no longer present and the triplet at τ 6.80 was found to be equal to the area of the signal at τ 7.10. The spectrum at this point is identical with that of bis(piperidino)alane (see Figure 3). These spectral data were found to be insensitive to further heating. The aluminum:hydrogen ratio was determined for an aliquot and found to be 1:1. A gray precipitate (assumed to be aluminum) formed during this pyrolysis. This spectral study of the aminoalane decomposition does show that the soluble species formed is bis(piperidino)alane and that the pyrolysis reaction stops with formation of this species. We propose the following pyrolysis reaction to account for these data

$$2H_2AlNC_5H_{10} \longrightarrow HAl(NC_5H_{10})_2 + {}^3/_2H_2\uparrow + Al\uparrow \quad (8)$$

Attempts were made to obtain quantitative characterization of this conversion by employing simultaneous gravimetric and differential thermal analysis. Dta–tga data obtained for mono- and bis(piperidino)-alanes are shown in Figure 2. The dta of piperidinoalane exhibited three *endothermic* effects at 60, 195, and 310°. The first is assigned to melting and corresponds to the reported melting point of 58°. The effect at

(12) E. Wiberg, M. Schmidt, and U. R. Uson, *Z. Naturforsch. B*, **6**, 393 (1951).

195° is tentatively assigned to the decomposition of piperidinoalane to bis(piperidino)alane, aluminum, and hydrogen; however, the weight loss at this point (curve B) was always found to be greater (by ~50%) than that predicted on the basis of the proposed pyrolysis reaction. Some material, however, was always found to "blow" out of the crucible and observed to collect on the inner surface of the furnace assembly. It was found that this extraneous weight loss could be diminished by using a crucible cover and heating at a slower rate, but it could never be eliminated completely. The last endotherm (310°) is assigned to decomposition of bis(piperidino)alane. This assignment is verified by the thermogram obtained for bis(piperidino)alane (C) which exhibited, in addition to endothermic melting at 100°, a similar decomposition endotherm at 310°. (The tga trace (D) indicates only *one* weight loss for bis(piperidino)alane which most logically corresponds to the endotherm at 310°.)

A sealed-tube pyrolysis experiment was performed in order to gain more information about the endothermic transition at ~200°. Hydrogen (0.755 mmol) was obtained when piperidinoalane (1.10 mmol) was heated at 200° for 15 min in a sealed tube. This is 90% of the calculated amount based on eq 8. The proton magnetic resonance spectrum of the benzene-soluble pyrolysate was found to be identical with that of authentic bis(piperidino)alane. These data are taken as verification of the proposed pyrolysis.

The conversion of dialkylaminoalanes to the corresponding bis(dialkylamino)alane appears to be a perfectly general reaction as evidenced by dta–tga studies of diethylamino- and pyrrolidinoalane (Table IV).

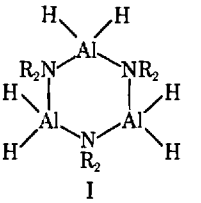
TABLE IV
THERMAL PROPERTIES OF AMINOALANES AS DETERMINED BY DTA–TGA ANALYSIS

Compd	Temp of dta effect (endotherm), °C	Assignment
$H_2AlN(C_2H_5)_2$	30	Melting
	180	Formn of $HAl(N(C_2H_5)_2)_2$, Al, and H_2
	240	Decompn of $HAl(N(C_2H_5)_2)_2$
$HAl(N(C_2H_5)_2)_2$	240	Decompn of $HAl(N(C_2H_5)_2)_2$
$H_2AlNC_4H_8$	90	Melting
	150	Formn of $HAl(NC_4H_8)_2$ + Al + H_2
	305	Decompn of $HAl(NC_4H_8)_2$
$HAl(NC_4H_8)_2$	300	Decompn of $HAl(NC_4H_8)_2$
$H_2AlNC_5H_{10}$	60	Melting
	195	Formn of $HAl(NC_5H_{10})_2$, Al, and H_2
	310	Decompn of $HAl(NC_5H_{10})_2$
$HAl(NC_5H_{10})_2$	100	Melting
	310	Decompn of $HAl(NC_5H_{10})_2$

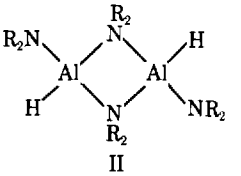
The dta trace of diethylaminoalane showed endothermic effects at 30, 180, and 240° (Table IV). These effects are assigned to melting of the starting material, thermal decomposition according to eq 8, and decomposition of bis(diethylamino)alane, respectively. Verification of the assignment of the effect occurring at 240° was obtained from dta–tga analysis of bis(diethylamino)alane which showed a similar decomposition endotherm at 240°. The weight loss accompanying the effect occurring at 180° was always greater than that predicted on the basis of eq 8. This we believe is due to extraneous weight loss due to excessive "bumping" of the material which was mentioned earlier. Quantitative characterization of this reaction was obtained by heating diethylaminoalane in an evacuated, sealed tube at 180° followed by analysis for hydrogen. Hydrogen (0.965 mmol) was obtained from 1.52 mmol of diethylaminoalane under these conditions. This is 90% of the calculated amount based on eq 8. Pyrrolidinoalane decomposes in an analogous fashion. Three endothermic effects (Table IV) at 90, 150, and 305° were observed. These are assigned to melting of the reagent, decomposition according to eq 8, and decomposition of bis(pyrrolidino)alane, respectively. Bis(pyrrolidino)alane exhibited a similar decomposition endotherm at 300°.

These pyrolyses confirm conclusions based on our studies of the direct synthesis of aminoalanes and in particular on our inability to prepare the dialkylaminoalanes in high yield. Dialkylaminoalanes have been shown to decompose according to reaction 8 slowly by refluxing in hydrocarbon solvent and rapidly by heating the neat material at the decomposition temperature.

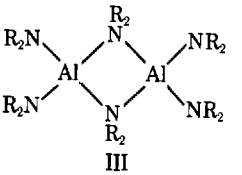
Spectroscopic Studies of Aminoalanes.—Aminoalanes are associated in hydrocarbon solution. Dialkylaminoalanes are trimeric in benzene while the corresponding bis(dialkylamino)alanes are mainly dimeric.[8] The smaller degree of association of the bis(dialkylamino)alanes is undoubtedly a result of greater steric crowding in the more highly substituted alane derivatives. Tris(dimethylamino)alane is the only known tris(amino)alane which is associated in benzene, that being as a dimer. Aminoalanes could conceivably associate with formation of NR_2 or H bridges; the latter is improbable since dimerization through coordinatively bonded amino groups is considerably more favored thermodynamically over an Al–H–Al three-centered bridge bond. The most logical structures for the aminoalanes based on these general considerations are I–III. In addition, these structures are consistent with those which have been demonstrated for homologous aminoboranes[13] and proposed for alkoxyalanes[14] on the basis of X-ray, nmr, infrared, and dipole moment studies.



I
dialkylaminoalane



II
bis(dialkylamino)alane



III
tris(dialkylamino)alane

The expected range for the Al–H stretching vibration[15] is 1600–1900 cm^{-1}, with a bridging hydride showing a relatively broad band around 1600 cm^{-1}. An increase in coordination on the aluminum atom normally shifts the Al–H bands to lower frequency. Sub-

(13) L. M. Trefonas and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **81**, 4435 (1959).
(14) H. Nöth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 44 (1968).
(15) H. M. Alpatova, T. N. Dymova, Yu. M. Kessler, and Om. R. Osipov, *Russ. Chem. Rev.*, **37**, 99 (1968).

stitution of hydride hydrogen atoms by electronegative substituents strengthens the Al–H bond as a consequence of inductive effects.

The Al–H stretching vibration for the dialkylaminoalanes (neat or in solution) occurs at ~1830 cm^{-1} (Table V). The Al–H deformation frequencies ranged from 725 to 735 cm^{-1}. The position of these bands suggests a tetravalent aluminum with hydrogen atoms bonded in *terminal* positions, in support of the amino-bridged structure (I). The proton magnetic resonance spectral data are also in support of this structure. The dialkylaminoalanes exhibited only one kind of hydridic hydrogen and dialkylamino environment (Table VI).

TABLE V
INFRARED SPECTRAL DATA OF AMINOALANES

Compd	Al–H str freq, cm^{-1}	Al–H def freq, cm^{-1}	Compd	Al–H str freq, cm^{-1}	Al–N def freq, cm^{-1}
$HAl(N(CH_3)_2)_2$	1824	...	$HAl(NC_4H_8)_2$	1824	695
$H_2AlN(C_2H_5)_2$	1829	734	$H_2AlNC_5H_{10}$	1828	725
$HAl(N(C_2H_5)_2)_2$	1822	692	$HAl(NC_5H_{10})_2$	1825	688
$H_2AlNC_4H_8$	1832	729			

The Al–H stretching frequencies of the bis(dialkylamino)alanes (neat or in solution) occur in the range 1822–1830 cm^{-1} (Table V). Absorption in this region is indicative of four-coordinate aluminum with Al–H bonds in terminal positions, in accord with structure II. The proton magnetic resonance spectra of the bis(dialkylamino)alanes showed only one hydridic environment (when this could be observed) and two nonequivalent dialkylamino environments of equal intensity. These data are also consistent with structure II. Specifically, bis(dimethylamino)alane exhibited proton signals at τ 6.17, 7.19, and 7.67 of relative areas 1.6:6.0:6.0 (Figure 4). These are assigned to hydridic hydrogen, terminal, and bridging dimethylamino environments, respectively. The dimethylamino resonances were assigned by reference to the spectrum of dimeric tris(dimethylamino)alane (Figure 4) in benzene which shows terminal and bridging dimethylamino signals at τ 7.23 and 7.51, respectively (relative area ratios 2.0:1.0, respectively). The spectral assignment for bis(piperidino)alane is a bit more complex owing to the presence of nitrogen α-, β-, and γ-methylene environments. The spectrum of this compound in benzene solution consisted of signals at τ 6.80 (triplet), 7.10 (triplet), and 8.43 (complex multiplet) of relative areas 1.0:1.0:3.0, respectively (Figure 3). These are assigned to terminal nitrogen α-methylene, bridging nitrogen α-methylene, and superimposition of both terminal and bridging nitrogen β- and γ-methylene protons, respectively. Resonance of the hydridic proton was not observed.

TABLE VI
PROTON MAGNETIC RESONANCE SPECTRAL PARAMETERS OF AMINOALANES IN BENZENE

Compd	i	τ	Multiplicity	Rel area	Assignment
$H_2AlN(CH_3)_2$	2.9	4.2	Singlet	...	Al–H
		5.9	Singlet	...	Nitrogen methyl
$HAlN(CH_3)_2$	2.4	6.17	Singlet	1.0	Al–H
		7.19	Singlet	6.0	Terminal dimethylamino
		7.67	Singlet	6.0	Bridging dimethylamino
$Al(N(CH_3)_2)_3$	2.2	7.23	Singlet	2.0	Terminal dimethylamino
		7.51	Singlet	1.0	Bridging dimethylamino
$H_2AlNC_5H_{10}$	2.4	5.76	Singlet	1.0	Al–H
		7.13	Triplet	1.1	Bridging nitrogen α-methylene proton
		8.63	Multiplet	3.2	Bridging nitrogen β- and γ-methylene protons
$HAl(NC_5H_{10})_2$	2.2	6.80	Triplet	1.0	Terminal nitrogen α-methylene proton
		7.10	Triplet	2.0	Bridging nitrogen α-methylene proton
		8.43	Multiplet	3.0	Superimposition of terminal and bridging nitrogen β- and γ-methylene protons
$H_2AlNC_4H_8$	3.0	6.79	Triplet	1.0	Bridging nitrogen α-methylene proton
		8.32	Triplet	1.0	Bridging nitrogen β-methylene proton
$HAl(NC_4H_8)_2$	2	6.69	Triplet	1.0	Terminal nitrogen α-methylene proton
		6.99	Triplet	1.0	Bridging nitrogen α-methylene proton
		8.29	Multiplet	2.0	Terminal and bridging nitrogen β-methylene proton
$HAl(N(C_2H_5)_2)_2$	...	~6.9	Multiplet	2.0	Ethyl–methylene
		~8.8	Multiplet	3.0	Ethyl–methyl
$H_2AlN(C_2H_5)_2$	2.1	6.83	Quartet	2.0	Ethyl–methylene
		8.84	Triplet	3.0	Ethyl–methyl
$H_3AlN(CH_3)_3$	1.4	5.80	Singlet	1.0	Al–H
		7.96	Singlet	3.0	Nitrogen methyl

The proton magnetic resonance spectrum of piperidinoalane is shown in Figure 3. The signals at τ 5.76 (singlet), 7.13 (triplet), and 8.63 (multiplet) of relative intensities 1.0:2.1:3.2 are assigned to hydridic hydrogen, bridging nitrogen α-methylene, and superimposition of bridging nitrogen β- and γ-methylene protons, respectively. It occurred to us that the hydride resonance appears at an abnormally low chemical shift for a main group metal hydride; however, the compounds R_2AlH[16] and $H_3AlN(CH_3)_3$ were found to exhibit hydride signals at τ 6.3 and 5.8, respectively. Proton magnetic resonance spectra of the remaining dialkylaminoalanes (Table VI) are also consistent with structure I, although a hydride resonance was not observed for all of these. The absence of a visible hydride resonance is probably due to the extensive broadening by the relatively large electric quadrupole moment associated with the ^{27}Al nucleus.

The proton magnetic resonance spectrum of bis(diethylamino)alane was the most complex and requires detailed explanation (Figure 5). The spectrum is consistent with a dimer of structure II but is complicated by fortuitous overlap of bridging and terminal nitrogen methylene quartets and methyl triplets. Two fairly distinct methylene quartets of approximately equal area are resolved; however, the signals for the

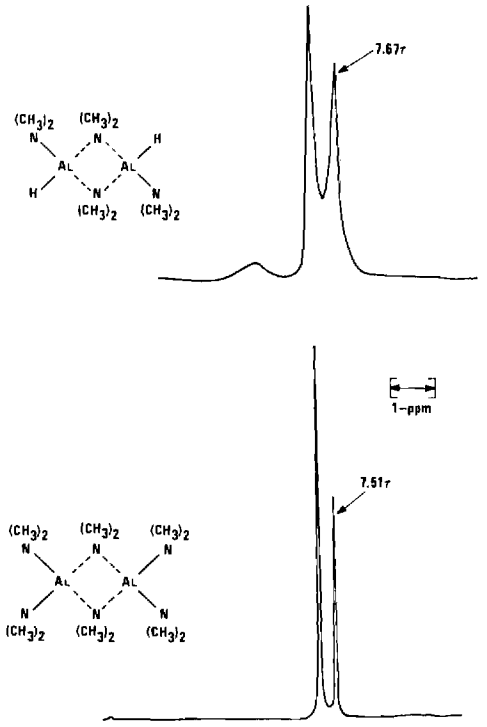


Figure 4.—Proton magnetic resonance spectra of bis- and tris(dimethylamino)alane in benzene solution.

methyl groups appear as a 1:4:4:1 quartet. This is presumably due to overlapping of both the central- and high-field components of one methyl triplet with the central- and low-field components of the other. A 1:4:4:1 quartet is predicted if the two triplet signals which overlap are each present in equal intensity.

In summary, this work provides a reasonably detailed study of the direct synthesis of aminoalanes by the reaction of aluminum, hydrogen, and secondary amines. Although bis- and tris(dialkylamino)alanes were synthesized in high yields, dialkylaminoalanes could be prepared only in modest yield due to the thermal instability of these compounds. Spectroscopic data (infrared and proton nmr) were compiled for these compounds and used to (1) characterize reaction products, (2) monitor pyrolysis reactions, and (3) provide structural information.

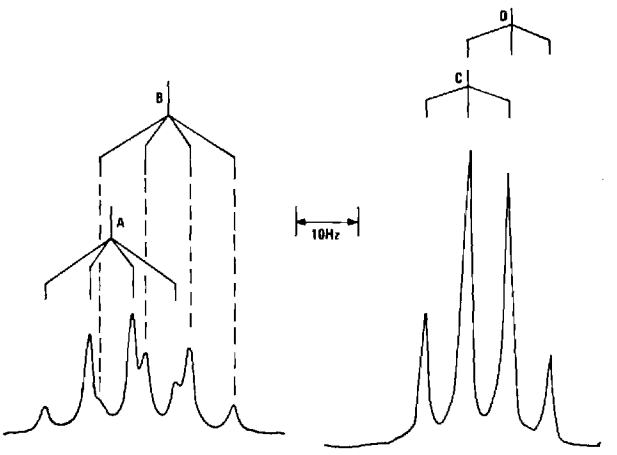


Figure 5.—Expanded-scale proton magnetic resonance spectrum of bis(diethylamino)alane in benzene solution: A, methylene quartet at τ 6.80; B, methylene quartet at τ 6.93; C, methyl triplet at τ 8.77; D, methyl triplet at τ 8.91.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. NOOO 14-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

[Reprinted from Inorganic Chemistry, 10, 900 (1971).]

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A Convenient Synthesis of Aminoboranes

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Received August 20, 1970

Detailed studies of the synthesis of aminoboranes by the reduction of phenyl borate with aluminum and hydrogen in the presence of secondary amines have been carried out. The amines used were diethylamine, diisopropylamine, and piperidine and the nature of the product formed was found to be a function of the phenyl borate:amine ratio. For example, tris(diethylamino)borane (81%) is prepared in admixture with bis(diethylamino)borane (5%) when diethylamine is used as the solvent whereas bis(diethylamino)borane is prepared exclusively and in high yield (80%) when phenyl borate and diethylamine are employed in a 1:2 molar ratio in benzene solvent. Aluminum–hydrogen reduction of equimolar quantities of phenyl borate and diethylamine in benzene solvent did not afford a high yield of the expected diethylaminoborane. Instead, nearly equimolar quantities of diethylaminohydridophenoxyborane [$HB(OC_6H_5)N(C_2H_5)_2$] and diethylaminobis(phenoxy)borane [$B(OC_6H_5)_2N(C_2H_5)_2$] were isolated. This reaction was found to be insensitive to changes in reaction time or temperature. The reaction sequence proposed to explain formation of the latter products involves (1) intermediate formation of AlH_3 [$Al + {}^3/_2H_2 \rightarrow AlH_3$], (2) reaction between AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)alane

$$AlH_3 + R_2NH \longrightarrow AlH_3NR_2H \xrightarrow[-H_2]{} H_2AlNR_2 \xrightarrow[-H_2]{R_2NH} HAl(NR_2)_2$$

and (3) reduction of phenyl borate by bis(diethylamino)alane [$2B(OC_6H_5)_3 + HAl(NR_2)_2 \rightarrow HB(OC_6H_5)NR_2 + B(OC_6H_5)_2NR_2 + Al(OC_6H_5)_3$]. Exchange studies between a number of aminoalanes and borate esters were also carried out.

Introduction

The use of aminoboranes as catalysts,[1] reducing agents,[2] and synthetic intermediates[3] has been reported; however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoboranes have been prepared by the reaction of diborane with secondary amines[4] (eq 1) or of an alkali metal borohydride with a dialkylammonium chloride[5] (eq 2).

$$B_2H_6 + 2HNR_2 \longrightarrow 2H_3BNR_2H \xrightarrow[-2H_2]{} 2H_2BNR_2 \quad (1)$$

$$NaBH_4 + R_2NH_2{}^+Cl^- \longrightarrow H_3BNR_2H + NaCl + H_2 \xrightarrow[-H_2]{} H_2BNR_2 \quad (2)$$

More recently the aluminum–hydrogen system has been used to arrive at a more economic and convenient route to precursors of aminoboranes. In this connection it has been found that aluminum and hydrogen reduces (1) boric oxide in the presence of aluminum chloride to form diborane in 40–50% yield at 750 atm[6] (eq 3), (2) methyl borate (in the presence of an $AlCl_3$–NaCl melt) to form B_2H_6 in ~20–30% yield,[7] and (3) phenyl borate (in the presence of tertiary amines) to form amine–boranes in nearly quantitative yield (eq 4).[8] In the latter case, the soluble amine–boranes were easily separated from the insoluble aluminum phenoxide byproduct by filtration. The reduction of phenyl borate

$$6(AlH_xCl_{3-x}) + xB_2O_3 \longrightarrow xB_2H_6 + 6AlO_{x/2}Cl_{3-x} \quad (3)$$

$$B(OC_6H_5)_3 + {}^3/_2H_2 + NR_3 + Al \longrightarrow H_3BNR_3 + Al(OC_6H_5)_3 \quad (4)$$

by aluminum and hydrogen in the presence of tertiary amines represents a convenient route to amine–boranes which is probably also the most economic route to this class of compounds. The reaction is thought to proceed through the intermediate formation of AlH_3 followed by reduction of the phenyl borate to diborane which then reacts with the tertiary amine to form the amine–borane. The reduction of phenyl borate with aluminum and hydrogen in the presence of an equimolar amount of a secondary amine was predicted in an analogous way to generate dialkylamine–boranes (eq 5). Unfortunately dialkylamine–boranes are only stable at low temperatures;[9] however when the reaction is carried out in 1:1, 1:2, and 1:3 stoichiometry (phenyl borate:amine) under the conditions of Al–H_2 reduction (120–160°), it should be possible to form dialkylaminoboranes (H_2BNR_2), bis(dialkylamino)boranes ($HB(NR_2)_2$), and tris(dialkylamino)boranes [$B(NR_2)_3$] (eq 6).

$$B(OC_6H_5)_3 + Al + {}^3/_2H_2 + HNR_2 \xrightarrow{100\text{–}150^\circ} \underset{H}{H_3B\cdot NR_2} + Al(OC_6H_5)_3 \quad (5)$$

$$\underset{H}{H_3B\cdot NR_2} \xrightarrow[-H_2]{} H_2BNR_2 \xrightarrow[-H_2]{HNR_2} HB(NR_2)_2 \xrightarrow[-H_2]{HNR_2} B(NR_2)_3 \quad (6)$$

Thus, it should be possible to synthesize a wide variety of aminoboranes depending on the initial stoichiometry of the reactants and the reaction temperature. The economics of these processes are worthy of note since the raw materials are borax, aluminum, and hydrogen. The final products are aminoboranes and aluminum phenoxide which can easily be separated by filtration of the insoluble aluminum phenoxide. Hydrolysis of the aluminum phenoxide in the presence of sulfuric acid regenerates phenol and forms alum ($Al_2(SO_4)_3$) (a seizing material used in the paper industry). The regenerated phenol can then react with borax and H_2SO_4 to form more phenyl borate.

$$B(OC_6H_5)_3 + Al + H_2 \xrightarrow{R_2NH} H_3BNR_2H + Al(OC_6H_5)_3 \quad (7)$$

borax + H_2SO_4 ; H_2SO_4 ; $C_6H_5OH + Al_2(SO_4)_3$

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(2) B. M. Mikhailov and V. A. Dorakhov, *Dokl. Chem.*, **136**, 51 (1961).
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The present study was undertaken to establish procedures for preparing exclusively, in high yield, each of the predicted reaction products. Description of the course of the aluminum–hydrogen–phenyl borate reduction was of additional interest and experiments were conducted to describe the reaction sequence involved.

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of either standard bench-top techniques carried out under a dry nitrogen atmosphere or in a drybox equipped with an atmosphere purification system for removal of oxygen and moisture.[10] Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained from the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using solvent signals (either benzene or methylene dichloride) as the internal standard.

Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave unit from Autoclave Engineers Inc. The chamber was charged in the drybox, and the contents were heated with stirring under hydrogen for a predetermined time. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum and aluminum phenoxide in the drybox.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from $NaAlH_4$ prior to use. Diethylamine was purchased from Eastman Chemicals and distilled onto active molecular sieve, Type 4-A. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. The aluminum was "activated" prior to use by a modification of the method described by Ziegler.[11] Boric acid and phenol were obtained from Fisher Chemical Co. and used without further purification. Phenyl borate was prepared by the reaction of boric acid and phenol according to the method described by Lappert and coworkers.[12] Ultra Pure hydrogen (99.9995%) was obtained from the Matheson Corp. and used without further purification.

Analyses.—Aminoboranes are relatively stable toward hydrolysis.[13] Complete hydrolysis was effected by boiling in water for extended periods (several hours). Samples for analysis were weighed in 50–100-ml flasks, attached to a distillation column, and 50 ml of distilled water was added. The mixtures were heated to distil the evolved amine into a receiver kept cold with a water–ice slurry. Nitrogen (as secondary amine) in the distillate was determined by titration with standard acid. Boron was determined by standard base titration of the boric acid–mannitol complex.[14] The unsymmetrical dialkylaminohydridophenoxyboranes [$HB(OC_6H_5)NR_2$, R = C_2H_5 and i-C_3H_7] were analyzed by a modification of the above procedure. Boron was separated from phenol (after hydrolysis and removal of the amine by distillation) by distillation of boron as methyl borate.[15] Boron was analyzed in the distillate as described above.

Hydrogen in these compounds was not measured analytically owing to the difficulty of effecting complete hydrolysis on a hydrogen gas liberation manifold. The presence of hydrogen (or absence) was determined qualitatively by infrared spectral techniques.

Reactions: Aluminum–Hydrogen Reductions of Phenyl Borate. A. Preparation of Bis(diethylamino)borane.—In a typical experiment phenyl borate (30 g or 0.1 mol), diethylamine (0.2 mol), aluminum metal (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 180° under 3000 psig of hydrogen for 5 hr (reaction 2, Table I). Vacuum distillation (after filtration of the reaction mixture to remove unreacted aluminum metal and aluminum phenoxide and removal of benzene solvent under vacuum) gave a single fraction which boiled at 62° (15.0 mm). The yield of bis(diethylamino)borane was 13.3 g or 85%. *Anal.* Calcd for $HB(N(C_2H_5)_2)_2$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3. Aluminum phenoxide (~15 g) (determined by comparison of infrared spectral data) was left in the distillation flask.

B. Preparation of Tris(diethylamino)borane.—Phenyl borate (0.1 mol), aluminum metal (2.7 g or 0.1 g-atom), and diethylamine (as solvent, 100 ml) were heated at 180° under 3000 psig of hydrogen for 24 hr (reaction 1, Table I). Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. Bis(diethylamino)borane distilled at 63° (15 mm, yield 5%) and tris(diethylamino)borane distilled at 95° (11 mm, 81% yield). *Anal.* Calcd for $B(N(C_2H_5)_2)_3$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3.

C. Attempted Preparation of Diethylaminoborane.—Phenyl borate (0.1 mol), diethylamine (0.1 mol), aluminum metal (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 180° under 3000 psi of hydrogen for 2 hr (eq 5, Table I). Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. The first fraction, $HB(OC_6H_5)N(C_2H_5)_2$ (42% yield), distilled at 90° (5 mm) while the second fraction, $B(OC_6H_5)_2N(C_2H_5)_2$ (39% yield), distilled at 120° (0.5 mm). *Anal.* Calcd for $HB(OC_6H_5)N(C_2H_5)_2$: B, 6.11; N (as amine), 40.6. Found: B, 6.12; N, 40.2. Infrared spectral analysis indicated both aromatic, *N*-alkyl, and active hydride environments (B–H at 2498 cm^{-1}). Proton magnetic resonance spectroscopic analysis (in CH_2Cl_2) showed signals at τ 2.87 (aromatic multiplet), 6.76 (ethylmethylene quartet), and 8.80 (ethylmethyl triplet) of relative areas 4.7:4.0:6.2, respectively. *Anal.* Calcd for $B(OC_6H_5)_2N(C_2H_5)_2$: B, 4.02; N (as amine), 26.8. Found: B, 3.82; N, 25.6. Infrared spectral analysis indicated the absence of a B–H stretching band and the presence of both aromatic and *N*-alkyl environments. The proton magnetic resonance spectrum of this compound in CH_2Cl_2 consisted of signals at τ 3.07 (aromatic multiplet), 6.86 (ethylmethylene quartet), and 8.86 (ethylmethyl triplet) of relative areas 10.0:3.7:6.2, respectively.

Essentially the same results were observed when the reaction time was extended to 4 and 24 hr (reactions 6–8, Table I) with the exception that in each case a small quantity (<1% yield) of $H_2B[N(C_2H_5)_2]$ vapor transferred (at 25°, 0.25 mm) into a Schlenk tube cooled in a Dry Ice–acetone slurry prior to vacuum distillation of the major components as described above. The infrared spectrum of this material (Nujol mull) was identical with that of $H_2B[N(C_2H_5)_2]$ prepared by unequivocal synthesis (*vide infra*). The observed melting point of 44° corresponds to the literature value.[16]

D. Synthesis of Bis(piperidino)borane.—Phenyl borate (0.1 mol), piperidine (0.2 mol), aluminum (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 150° under 4000 psig of hydrogen for 12 hr (reaction 3, Table I). The reaction mixture was filtered in the drybox and solvent was removed *in vacuo*. Vacuum distillation of the residue gave one fraction which boiled at 95° at 5 mm. The infrared spectrum of this material (neat between KBr plates) exhibited a B–H stretching frequency at ~2500 cm^{-1}. The proton magnetic resonance spectrum in CH_2Cl_2 indicated the absence of aromatic absorption and the normal resonances characteristic of free piperidine. Analysis of this material revealed an amine:boron ratio of 1.92:1.00 indicating that the compound is bis(piperidino)borane; yield 12 g or 67%. *Anal.* Calcd for bis(piperidino)borane: B, 6.12; amine, 93.4. Found: B, 6.11; amine, 92.1.

E. Attempted Synthesis of Bis(diisopropylamino)borane.—Phenyl borate (0.1 mol), diisopropylamine (0.20 mol), aluminum (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 150° under 4000 psig of hydrogen for 5 hr (reaction 4, Table I). After cooling, the mixture was filtered and the solvent was removed from the filtrate *in vacuo*. Vacuum distillation of the residue gave two fractions. The first fraction boiled at 90° (0.5 mm) and was found to be diisopropylaminohydridophenoxyborane [$HB(OC_6H_5)N(i\text{-}C_3H_7)_2$]. *Anal.* Calcd for diisopropylaminohydridophenoxyborane: B, 5.54; amine, 51.3. Found: B, 5.29; amine, 47.3. The infrared spectrum of this material exhibited a B–H stretching frequency at 2502 cm^{-1}. The proton magnetic resonance spectrum was complex and will be discussed in detail in the Discussion. The spectrum of this material, dis-

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solved in CH_2Cl_2, revealed aromatic and nitrogen isopropyl proton resonances in the expected ratio of 5:14. The 40° spectrum of the nitrogen–alkyl region of the neat material (with trace toluene as internal standard) is shown in Figure 1 while the spectrum obtained at 120° is shown in Figure 2.

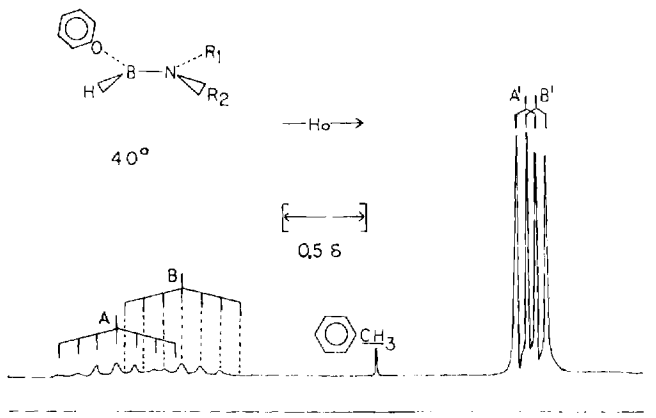

Figure 1.—Nitrogen alkyl proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane at 40°: A, methyne septet at τ 6.20; B, methyne septet at τ 6.62; A′, doublet at τ 8.72; B′, doublet at τ 8.82. $CH_3C_6H_5$ is the internal standard.

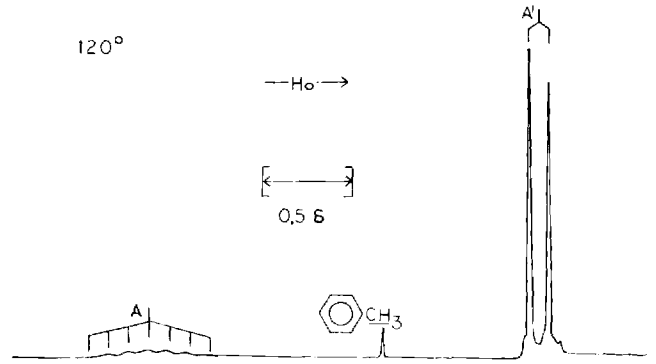

Figure 2.—Proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane at 120°: A, methyne septet at τ 6.42; A′, doublet at τ 8.71. $CH_3C_6H_5$ is the internal standard.

The second fraction boiled at 125° (0.5 mm). There was no band in the infrared spectrum of this fraction indicative of a B–H environment. The proton magnetic resonance spectrum of the neat material indicated aromatic and nitrogen isopropyl proton environments in the ratio of 10:14, indicating that the material has the empirical formula $B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$. *Anal.* Calcd for $B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$: B, 3.7. Found: B, 3.9.

F. Aluminum–Hydrogen Reduction of Methyl Borate.—Methyl borate (0.1 mol from Aldrich Chemical Corp. and distilled from sodium metal), diethylamine (0.2 mol), aluminum, (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 140° under 4000 psig of hydrogen for 5 hr. This mixture was cooled, vented, and filtered in the drybox. The proton magnetic resonance spectrum of the filtrate matched exactly that of an equimolar mixture of methyl borate and diethylamine in benzene. No aluminum was found in solution, indicating that no reaction had occurred. Similar results were observed in analogous experiments when the reaction time was extended to 24 hr or at reaction temperatures of 100–180°.

Aminoalane–Borate Ester Exchange Reactions. A. Reaction of Equimolar Quantities of Bis(diethylamino)alane and Phenyl Borate.—Phenyl borate (2.89 g or 0.0100 mol) and bis(diethylamino)alane (1.707 g or 0.00995 mol) prepared by the direct reaction of aluminum, hydrogen, and diethylamine[17] at 180° were weighed and mixed in the drybox (reaction 1, Table II). Immediate evolution of heat was accompanied by solution of the phenyl borate. The infrared spectrum (neat) showed a B–H stretching vibration at 2500 cm^{-1} but no Al–H stretching bands. Benzene (25 ml) was added and the mixture was stirred at 55° for 12 hr. A white precipitate (later identified as aluminum phenoxide by comparison of infrared spectral data) had formed. The mixture was filtered, solvent was removed under vacuum, and the product was separated by vacuum distillation. The product boiled at 63° (15 mm) and was identified as $HB[N(C_2H_5)_2]_2$ by comparison of infrared spectral data. The yield was 1.5 g or 96% recovery of boron. Some 1.8 g of aluminum phenoxide remained in the distillation flask.

B. Reaction of Phenyl Borate and a 0.5 Molar Equiv of Bis(diethylamino)alane.—Phenyl borate (9.2 g or 0.0318 mol) and bis(diethylamino)alane[19] (2.74 g or 0.0159 mol) were mixed in 25 ml of benzene. Evolution of heat was noted. The mixture was stirred for 12 hr at 55°. White solid (later identified as aluminum phenoxide by infrared spectral comparison) formed during this period. The solution was filtered and the solvent was removed under vacuum. Vacuum distillation gave two products, $HB(OC_6H_5)N(C_2H_5)_2$ at 90° (5 mm) (2.87 g or 0.0162 mol) and $B(OC_6H_5)_2N(C_2H_5)_2$ at 120° (0.5 mm) (2.69 g or 0.0101 mol). These products were identified by comparison of appropriate infrared spectral data. Some aluminum phenoxide remained in the distillation flask. Aluminum phenoxide obtained in both the filtration and distillation steps was combined and the yield found to be 5.629 or 0.0184 mol.

C. Reaction of Equimolar Quantities of Diethylaminoalane and Phenyl Borate.—Phenyl borate (10 mmol) and diethylaminoalane (10 mmol from the reaction of equimolar quantities of diethylamine and trimethylamine–alane in benzene solution) were mixed in benzene (25 ml) (reaction 2, Table II). The mixture was stirred at 60° for 12 hr during which time a white solid (later identified as aluminum phenoxide) had formed. The mixture was filtered and the solvent was removed from the filtrate under vacuum, yielding a volatile solid product. This was identified as diethylaminoborane by infrared spectral comparison. Some aluminum phenoxide remained in the distillation flask; yield 0.8 g or 94%.

D. Reaction of Equimolar Quantities of Methyl Borate and Bis(diethylamino)alane.—Methyl borate (1.14 ml or 10.0 mmol) was added to a stirred solution of bis(diethylamino)alane[19] (1.721 g or 10.0 mmol) in benzene (50 ml) (reaction 3, Table II). Solid formation (as a gel suspended in benzene) was rapid after approximately 30 sec. The mixture was filtered after 1 hr yielding a white solid and clear colorless filtrate. The solid was washed with additional benzene. The solvent was removed from the combined filtrates under vacuum yielding a relatively involatile liquid. This was shown to be bis(diethylamino)borane by infrared spectral comparison. The yield was 1.53 g or 9.8 mmol (98%).

E. Reaction of Equimolar Quantities of Methyl Borate and Diethylaminoalane.—Methyl borate (0.54 ml or 4.74 mmol) was added to a stirred solution of diethylaminoalane (0.04779 g or 4.74 mmol) in benzene (50 ml) (reaction 4, Table II). Solid formation was rapid (20 sec). The mixture was filtered after 5 hr yielding a white solid and a clear filtrate. Removal of solvent from the filtrate gave a white, volatile solid which was shown to be diethylaminoborane by infrared analysis. The diethylaminoborane was redissolved in benzene and made up to a known volume, and the yield was determined to be 91%.

F. Reaction of Equimolar Quantities of Methyl Borate and Bis(piperidino)alane.—Methyl borate (0.63 ml or 5.52 mmol) was added to a stirred solution of bis(piperidino)alane[18] (1.078 g or 5.52 mmol) in benzene (50 ml) (reaction 5, Table II). Formation of a solid was apparent after approximately 30 sec. This solid was separated by filtration yielding a clear colorless filtrate. Solvent was removed from the filtrate under vacuum yielding 0.915 g of a clear liquid material. This was found to be bis(piperidino)borane by analysis. *Anal.* Calcd for bis(piperidino)borane: B, 6.12; amine, 93.4. Found: B, 6.15; amine, 93.8 (yield 92%).

Unequivocal Synthesis of $H_3BN(C_2H_5)_2H$.—Diborane, generated by the reaction of $NaAlH_4$ and BF_3 in ether,[18] was passed through a trap cooled in a Dry Ice–acetone slurry and allowed to bubble through diethylamine in benzene. Isolation of liquid $H_3BN(C_2H_5)_2H$ was effected by removal of solvent under vacuum. *Anal.* Calcd for $H_3BN(C_2H_5)_2H$: B, 12.4; N (as amine), 84.0. Found: B, 12.6; N, 85.6. Infrared spectral analysis revealed N–H and B–H stretching frequencies at 3260 and 2330 cm^{-1}, respectively.

(18) A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, **71**, 3451 (1949).

TABLE I
PREPARATION OF AMINOBORANES BY ALUMINUM–HYDROGEN REDUCTION OF PHENYL BORATE (3000 PSI)

$$B(OC_6H_5)_3 + R_2NH + Al \xrightarrow[H_2]{\Delta} H_nB(NR_2)_{3-n} + Al(OC_6H_5)_3$$

Reaction no.	Amine	$B(OC_6H_5)_3$:amine molar ratio	Time, hr	Temp, °C	Products	Yield, %
1	Diethylamine	1:∞ (amine solvent)	24	180	$B[N(C_2H_5)_2]_3$	81
					$HB[N(C_2H_5)_2]_2$	5
2[a]	Diethylamine	1:2	5	180	$HB[N(C_2H_5)_2]_2$	85
3	Piperidine	1:2	12	150	$HB(NC_5H_{10})_2$	67
4	Diisopropylamine	1:2	5	150	$HB(OC_6H_5)N(i\text{-}C_3H_7)_2$	34
					$B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$	56
5[a]	Diethylamine	1:1	2	180	$HB(OC_6H_5)N(C_2H_5)_2$	42
					$BN(C_2H_5)_2(OC_6H_5)_2$	39
6	Diethylamine	1:1	4	180	$H_2BN(C_2H_5)_2$	<1
					$HB(OC_6H_5)N(C_2H_5)_2$	40
					$BN(C_2H_5)_2(OC_6H_5)_2$	35
7	Diethylamine	1:1	24	180	$H_2BN(C_2H_5)_2$	<1
					$HB(OC_6H_5)N(C_2H_5)_2$	38
					$BN(C_2H_5)_2(OC_6H_5)_2$	37
8	Diethylamine	1:1	24	100	$HB(OC_6H_5)N(C_2H_5)_2$	32
					$BN(C_2H_5)_2(OC_6H_5)_2$	47

[a] These results are each representative of three runs under the specified conditions.

Unequivocal Synthesis of $H_2BN(C_2H_5)_2$.—Diethylaminoborane was prepared by pyrolyzing $H_3BN(C_2H_5)_2H$ at 200° for 4 hr. The crystalline product melted at 44° (lit.[16] value 44°) and showed B–H stretching bands at 2422 and 2358 cm^{-1}. No N–H stretching band was visible.

Results and Discussion

Aluminum–Hydrogen Reduction of Borate Esters.—Reaction conditions and results of aluminum–hydrogen reduction of phenyl borate in the presence of a variety of secondary amines are summarized in Table I.

Reference to this table indicates that attempts to prepare tris(diethylamino)borane and bis(diethylamino)borane (reactions 1 and 2, respectively) were quite successful. In this connection bis(diethylamino)borane was prepared exclusively when aluminum and hydrogen were allowed to react with phenyl borate and 2 equiv of diethylamine. On the other hand, when diethylamine was used as solvent, tris(diethylamino)borane (81%) was generated in admixture with bis(diethylamino)borane (5%).

$$B(OC_6H_5)_3 + Al + H_2 + 2N(C_2H_5)_2H \longrightarrow HB[N(C_2H_5)_2]_2 + Al(OC_6H_5)_3 + {}^3/_2H_2 \quad (8)$$

$$B(OC_6H_5)_3 + Al + H_2 + 3N(C_2H_5)_2H \longrightarrow B[N(C_2H_5)_2]_3 + Al(OC_6H_5)_3 + {}^6/_2H_2 \quad (9)$$

The conditions for synthesis of bis(diethylamino)borane were extended to include direct preparation of bis(piperidino)- and bis(diisopropyl)aminoborane. Bis(piperidino)borane was generated in moderate yield (67%) in reaction 3, Table I, while markedly contrasting results were observed in the corresponding reaction with diisopropylamine (reaction 4, Table I). In this reaction none of the expected bis(diisopropylamino)borane could be isolated. Instead the reaction products were found to be diisopropylaminohydridophenoxyborane (yield 34%) and bis(phenoxy)diisopropylaminoborane (yield 56%).

Attempts to prepare diethylaminoborane exclusively and in high yield were not successful. Product analysis of reaction 5 (Table I) revealed formation of two compounds, $HB(OC_6H_5)N(C_2H_5)_2$ in 42% yield and $B(OC_6H_5)_2N(C_2H_5)_2$ in 39% yield.

$$2B(OC_6H_5)_3 + Al + H_2 + 2N(C_2H_5)_2H \longrightarrow HB(OC_6H_5)N(C_2H_5)_2 + B(OC_6H_5)_2N(C_2H_5)_2 + Al(OC_6H_5)_3 \quad (10)$$

Isolation of these products indicates incomplete reduction of the $B\text{–}OC_6H_5$ bonds and suggests that aluminum–hydrogen reduction of phenyl borate in the presence of *equal equivalents* of diethylamine involves a stepwise reduction. The initial results (reaction 5) suggest that additional reaction time is required in order to effect complete reduction necessary for the preparation of diethylaminoborane. In this connection, reaction times were extended to 4 and 24 hr (reactions 6 and 7). A low yield (<1%) of diethylaminoborane was isolated in each of these reactions; in addition, the major products (and respective yields) were found to be identical, within experimental error, to results observed when the reaction time was 2 hr. The same products were isolated even when the reaction temperature was lowered to 100° with a reaction time of 24 hr (reaction 8) indicating that failure to isolate diethylaminoborane is not due to thermodynamic instability of this material at higher temperatures.

Aminoalane Reductions of Borate Esters.—Inability to generate the expected diethylaminoborane by aluminum–hydrogen reductions of 1:1 molar mixtures of phenyl borate and diethylamine (reactions 5–8) and isolation of diethylaminohydridophenoxyborane and bis(phenoxy)diethylaminoborane in equal yields approximating 50% suggest a particular reaction sequence. Incomplete reduction of all phenoxyboron bonds suggests that (1) the active reducing agent is *not* an unlimited quantity of AlH_3 (generated by the reaction of excess Al and hydrogen) since AlH_3 would be expected to reduce phenyl borate to diborane, (2) the active reducing agent ("Al–H species") is present in limited quantity and functions only to reduce some of the phenyl borate, and (3) the quantity of actual reducing agent is limited by the quantity of secondary amine present initially.

The reaction sequence which is consistent with these general requirements and which we propose is the sequence operative in reactions 5–8 (Table I) involves (1) the intermediate formation of AlH_3 (by the reaction of aluminum and hydrogen, (2) reaction of AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)alane, and (3) reduction of phenyl borate by the aminoalane. The exact sequence pro-

posed is described below:
step I

$$2HNR_2 + Al \xrightarrow{H_2} HAl(NR_2)_2 \quad (11)$$

step II

$$2B(OC_6H_5)_3 + HAl(NR_2)_2 \longrightarrow HB(OC_6H_5)NR_2 + B(OC_6H_5)_2NR_2 + Al(OC_6H_5)_3 \quad (R = C_2H_5) \quad (12)$$

Independent verification of this reaction sequence has been obtained. With reference to step I we have found[17] that reaction of aluminum, hydrogen, and diethylamine in benzene solvent results in predominant formation of the corresponding bis(dialkylamino)alane by the reaction sequence shown in eq 13. It was demonstrated by dta–tga studies that bis(dialkylamino)alanes are more thermodynamically stable than the corresponding dialkylaminoalanes (H_2AlNR_2), and, thus, the former compounds are formed preferentially in this reaction. Prior art concerning step II is rather sparse. Some previous studies provide information concerning the reduction of borate esters with alkoxyalanes,[19] alanes, and alkali metal hydrides.[20] The reduction of borate esters with aminoalanes has not been studied in any detail; thus we attempted to study this reaction by characterizing the aminoalane reduction of phenyl borate at two different stoichiometries. In the first reaction, equimolar quantities of bis(diethylamino)alane and phenyl borate were allowed to react. Isolation of bis(diethylamino)boranes was nearly quantitative according to the reaction

$$Al + {}^3/_2H_2 \xrightarrow{HNR_2} H_3AlNR_2H \xrightarrow[-H_2]{} H_2AlNR_2 \xrightarrow[-H_2]{HNR_2} HAl(NR_2)_2 \quad (13)$$

$$B(OC_6H_5)_3 + HAl(NR_2)_2 \longrightarrow HB(NR_2)_2 + Al(OC_6H_5)_3 \quad (R = C_2H_5) \quad (14)$$

The infrared spectrum of the neat mixture obtained after initial mixing of the reagents exhibited a B–H stretching frequency at 2500 cm^{-1} and no Al–H stretching frequency. These data indicate that the first step of the exchange, transfer of hydrogen from aluminum to boron, occurs rapidly; however, the observation that "aluminum phenoxide" is dissolved in benzene (see Experimental Section) indicates that the intermediates actually present in this reaction are mixed, unsymmetrical $B(OC_6H_5)_n(NR_2)_{3-n}$ compounds (where $n = 1$ or 2). Equilibria among the species present allows isolation of the most volatile component [bis(diethylamino)borane] and forces the reaction to completion. These results indicate that aminoalanes exchange both hydrogen and secondary amino groups with phenyl borate when the aminoalane is present in sufficient quantity. The proposed stepwise reaction is

$$B(OC_6H_5)_3 + HAlNR_2 \longrightarrow HB(OC_6H_5)_2 + Al(NR_2)_2OC_6H_5 \rightleftharpoons HB(OC_6H_5)NR_2 + Al(OC_6H_5)_2NR_2 \rightleftharpoons HB(NR_2)_2 + Al(OC_6H_5)_3 \quad (15)$$

The reaction of phenyl borate and 0.5 molar equiv of bis(diethylamino)alane was studied to determine whether the incompletely exchanged boron species $HB(OC_6H_5)N(C_2H_5)_2$ and $B(OC_6H_5)_2N(C_2H_5)_2$ could be isolated when the aminoalane is present in limiting quantity. Infrared spectral analysis of the mixture obtained after initial mixing of the reagents indicates the absence of an Al–H stretching band and the presence of a B–H stretching band at ~2500 cm^{-1}. Thus, the first step of the exchange, transfer of hydride from aluminum to boron, occurs rapidly. Isolation of $HB(OC_6H_5)N(C_2H_5)_2$, $B(OC_6H_5)_2N(C_2H_5)_2$, and $Al(OC_6H_5)_3$ was nearly quantitative thus establishing the reaction sequence shown in eq 16 as a reasonable path in the proposed exchange reactions. Apparent solubilization of aluminum phenoxide in benzene is indicative of a complex equilibrium involving unsymmetrical, incompletely exchanged species. As before, the most volatile components (in this case $HB(OC_6H_5)N(C_2H_5)_2$ and $B(OC_6H_5)_2N(C_2H_5)_2$) were isolated by vacuum distillation.

$$\begin{array}{ccc} 2B(OC_6H_5)_3 + HAl(NR_2)_2 & \longrightarrow & HB(OC_6H_5)NR_2 + B(OC_6H_5)_2(NR_2) + Al(OC_6H_5)_3 \\ \downarrow & & \Downarrow \\ HB(OC_6H_5)_2 + Al(NR_2)_2OC_6H_5 + B(OC_6H_5)_3 & \rightleftharpoons & HB(OC_6H_5)NR_2 + Al(OC_6H_5)_2NR_2 + B(OC_6H_5)_3 \quad (R = C_2H_5) \end{array} \quad (16)$$

The results of the aminoalane–phenyl borate exchange reactions are in agreement with our observations concerning the reaction of equimolar mixtures of phenyl borate and diethylamine with aluminum and hydrogen. These exchange reactions successfully account for formation of the exact products (with analogous per cent yields) and in addition provide direct explanation of the apparent solubilization of aluminum phenoxide in benzene. These reactions provide convincing evidence that reactions of equimolar quantities of phenyl borate and diethylamine with aluminum and hydrogen proceed through intermediate formation of the bis(diethylamino)alane.

The aminoalane–borate ester reduction study was expanded to include the reaction of a greater variety of aminoalanes with phenyl borate and in addition the reaction of aminoalanes with methyl borate. The reactions studied and the results are summarized in Table II.

TABLE II
REACTION OF EQUIMOLAR QUANTITIES OF AMINOALANES WITH BORATE ESTERS IN BENZENE

$$H_nAl(NR_2)_{3-n} + B(OR')_3 \longrightarrow H_nB(NR_2)_{3-n} + Al(OR')_3$$

Reaction no.	NR_2	R'	n	Yield, %
1	$N(C_2H_5)_2$	C_6H_5	1	96
2	$N(C_2H_5)_2$	C_6H_5	2	94
3	$N(C_2H_5)_2$	CH_3	1	98
4	$N(C_2H_5)_2$	CH_3	2	91
5		CH_3	1	92

Reaction 1 was discussed above. Aminoalane reductions of methyl borate (reactions 3–5) proceed more cleanly than analogous reactions with phenyl borate in that precipitation of by-product aluminum methoxide is complete (presumably due to the higher heat of crystallization of this reagent) and the aminoborane is separated by simple filtration of the benzene solution. Reduction of borate esters by aminoalanes and synthesis of the corresponding aminoboranes appears to be a

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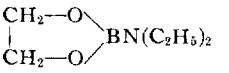
perfectly general reaction as evidenced by the successful synthesis of both diethylamino- and bis(diethylamino)-borane (reactions 1 and 2, respectively, involve phenyl borate while reactions 3 and 4, respectively, involve methyl borate). These reactions can logically be extended to include synthesis of the general series of aminoboranes as evidenced by the successful synthesis of bis(piperidino)borane from bis(piperidino)alane and trimethyl borate (reaction 5).

In view of our observations concerning the successful preparation of aminoboranes by aminoalane reductions of *methyl borate* we decided to substitute methyl borate for phenyl borate in the reaction with aluminum and hydrogen in the presence of a secondary amine. Such a substitution has obvious economic and practical merit since methyl borate is commercially available and phenyl borate is not. Surprisingly, no reaction of methyl borate with aluminum, hydrogen, and diethylamine under a variety of reaction conditions (see Experimental Section) was observed. This is an interesting observation in light of our earlier report that phenyl borate is reduced in high yield with aluminum and hydrogen in the presence of a tertiary amine to the amine–borane ($H_3B \cdot NR_3$) whereas the corresponding reaction using methyl borate does not take place. Since the bis(dialkylamino)alane reduces methyl borate to the bis(dialkylamino)borane, it is clear that the bis(dialkylamino)alane is not formed in the reaction of dialkylamines with aluminum and hydrogen with methyl borate although the reaction does occur with phenyl borate. It has been shown experimentally that no reaction at all takes place between methyl borate, diethylamine, aluminum, and hydrogen although the same reaction mixture minus methyl borate produces bis(diethylamino)alane in high yield. Thus it is clear that methyl borate or something contained in the methyl borate prevents reaction. A possible explanation involves the greater sensitivity of methyl borate to hydrolysis resulting in the formation of methyl alcohol which then deactivates the aluminum powder. The methyl borate used in these reactions was distilled over sodium and the reactions were carried out using precautions against atmospheric exposure; however it is possible that only minute contamination is needed to produce the observed effect.

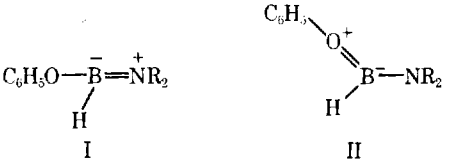
Properties of Dialkylaminohydridophenoxyboranes.—The dialkylaminohydridophenoxyboranes which were isolated have not been described previously. However, they are similar to analogous dialkylaminohydridothioboranes[21,22] which have been described. The dialkylaminohydridophenoxyboranes are liquids at room temperature and can be distilled under vacuum (see Experimental Section for details); they are stable to disproportionation up to their boiling points and are infinitely miscible with common hydrocarbon and ether solvents. They are hydrolyzed by water to hydrogen, boric acid, secondary amine, and phenol.

Ambient-temperature proton magnetic resonance spectra of the aminohydridophenoxyboranes are complex. In addition to normal phenoxy environments (and absence of hydride resonances) these compounds exhibit two nonequivalent nitrogen–alkyl environments of equal intensity. The alkyl region of the proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane is shown in Figure 1. Two partially overlapping septets (A and B centered at τ 6.62 and 6.20, respectively) and two doublets (A′ and B′ centered at 8.72 and τ 8.82, respectively) are clearly resolved at 40°.

Nonequivalent dialkylamino environments in these derivatives are most likely a result of boron–nitrogen π bonding and hindered rotation about this bond. That nonequivalence is not due to the existence of associated species was demonstrated by a magnetic resonance dilution study (spectra were recorded in benzene solution in the concentration range 1.0–0.05 *m*) which indicated that alkyl nonequivalence was independent of concentration. A variable-temperature study of the neat material (with trace toluene as internal standard) was performed. The resonances present in the 40° spectrum broadened with an increase in temperature. At 90° the resonances for the isopropyl methyl groups coalesced into a broad doublet while the methyne protons appeared as a broad (featureless) absorption at τ ~6.4. These signals were observed to sharpen as the temperature was raised. At 120° (Figure 2) the methyne protons appear as a distinct septet centered at τ 6.42 while the isopropyl methyl protons appear as a sharp doublet centered at τ 8.71. These spectra were found to be reversible. These spectral characteristics are very similar to those reported for $XB(NR_2)C_6H_5$ species (X = halogen, NCO; R = methyl, isopropyl) which were also interpreted in terms of nitrogen–boron π bonding and hindered rotation.[23,24] Boron–nitrogen π bonding in the aminohydridophenoxyboranes is interesting in view of possible competition with oxygen–boron π bonding. That boron–nitrogen π bonding is preferred when both are possible has also been suggested by infrared studies[25] in the system



and suggests that the resonance structure of type I is more important than that of type II.



I II

It is interesting to speculate on possible boron–nitrogen π bonding in the dialkylaminobis(phenoxy)borane derivatives which were isolated. No distinction is possible by nmr since B–N π bonding and coplanarity of the heavy-atom framework results in a plane of symmetry through boron and nitrogen and thus alkyl equivalence. In fact, proton magnetic resonance spectra of these derivatives ($B(OC_6H_5)_2NR_2$, R = C_2H_5 and *i*-C_3H_7) give rise to *single*, well-resolved *N*-alkyl signals at ambient temperature.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. NOOO 14-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

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[Reprinted from Inorganic Chemistry, **10**, 1524 (1971).]

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Synthesis of *N*-Trialkylborazines from Phenyl Borate, Aluminum, Hydrogen, and Primary Amines

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Received August 24, 1970

N-Trialkylborazines have received considerable attention in recent years and presently are utilized as synthetic intermediates[2,3] and as reducing agents.[4] Previously reported synthetic procedures involve reaction of diborane with primary amines[5] (eq 1), diborane with alkyl cyanides[6] (eq 2), and reaction of lithium borohydride and the appropriate monoalkylammonium halide[7] (eq 3).

$$B_2H_6 + 2H_2NR \xrightarrow{\Delta} {}^2/_3(HBNR)_3 + 4H_2 \quad (1)$$

$$B_2H_6 + 2RCN \xrightarrow{\Delta} {}^2/_3(HBNCH_2R)_3 \quad (2)$$

$$LiBH_4 + RNH_3{}^+Cl^- \xrightarrow{\Delta} LiCl + {}^1/_3(HBNR)_3 + 3H_2 \quad (3)$$

We have previously reported on the preparation of B–H compounds by the reduction of borate esters with aluminum and hydrogen. In this way amine–boranes[8] (eq 4) and aminoboranes[9] (equation 5) have been prepared in high yield. By analogy it would appear that reduction of phenyl borate with aluminum and hydrogen in the presence of a primary amine might produce borazines according to eq 6. In order to test this

$$B(OC_6H_5)_3 + Al + R_3N \xrightarrow[\Delta,\text{pressure}]{H_2} H_3BNR_3 + Al(OC_6H_5)_3 \quad (4)$$

$$B(OC_6H_5)_3 + Al + R_2NH \xrightarrow[\Delta,\text{pressure}]{H_2} HB(NR_2)_2 + Al(OC_6H_5)_3 \quad (5)$$

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \quad (6)$$

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idea phenyl borate was allowed to react with aluminum and hydrogen in the presence of primary amines under mild conditions of temperature and pressure. The success of this economic route to *N*-trialkylborazines should increase interest in this class of compounds considerably.

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by the use of standard Schlenk-tube techniques or by use of a drybox equipped with an atmosphere purification system for removal of oxygen and moisture.[10] Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained from analysis of the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using solvent signals (either benzene or methylene dichloride) as the internal standard. Mass spectra were obtained from analysis of the neat material using a Varian MS-66 instrument.

Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave unit obtained from Autoclave Engineers, Inc. The chamber was charged in the drybox, and the contents heated with stirring under hydrogen pressure for a predetermined period of time. A hydrogen pressure of 3000 psig was utilized since previous studies[9] have established the suitability of this reaction condition in the direct preparation of aminoborane compounds. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum and aluminum phenoxide in the drybox.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from $NaAlH_4$ prior to use. Monoethyl-, isopropyl-, and *tert*-butylamines were purchased from Eastman Chemical and dried over active molecular sieves, Type 4-A. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. The aluminum was "activated" prior to use by a modification of the Ziegler activation process.[11] Boric acid and phenol, used to prepare phenyl borate,[12] were obtained from Fisher Chemical and used without further purification.

Reaction of Ethylamine, Phenyl Borate, Aluminum, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), ethylamine (6.5 ml, 0.1 mol), phenyl borate (30 g, 0.1 mol), and benzene (100 ml) were heated at 150° under 3000 psig of hydrogen for 5 hr (reaction 1, Table I). The chamber was allowed to cool and was vented, and

TABLE I

PREPARATION OF *N*-TRIALKYLBORAZINES BY REDUCTION OF PHENYL BORATE WITH ALUMINUM AND HYDROGEN IN THE PRESENCE OF MONOALKYLAMINES

Reaction no.	R	Reaction time, hr	Reaction temp, °C	Product	Yield, %
1	C_2H_5	5	150	$(HBNC_2H_5)_3$	82
2	*i*-C_3H_7	12	150	$(HBN\text{-}i\text{-}C_3H_7)_3$	93
3	*tert*-C_4H_9	12	120	$(HBN\text{-}tert\text{-}C_4H_9)_3$	86

the benzene-soluble material was separated from unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid of low volatility. The infrared spectrum of this material (Nujol mull) revealed ν(B–H) (2490 cm^{-1}) and aromatic ν(C–H) ($\sim$>3000 cm^{-1}) in addition to "normal" alkyl C–C and N–C vibrations. *N*-Triethylborazine was collected in a Schlenk tube (cooled in a Dry Ice–acetone slurry) by heating at 200° under vacuum (0.25 mm). This left an undetermined amount of aluminum phenoxide (identified by comparison of infrared spectral data) as a residue. The borazine was purified by vacuum distillation (21° at 2.5 mm compared to the literature value[6] of 20° and 2.5 mm); yield 4.5 g, 82%. The purity and identity of the *N*-triethylborazine product were established by infrared, proton magnetic resonance, and mass spectral techniques. These data are compiled in Tables II–IV, respectively. The data are

TABLE II

N-TRIALKYLBORAZINE INFRARED SPECTRAL DATA

$(HBNC_2H_5)_3$[a]	$(HBN\text{-}i\text{-}C_3H_7)_3$[a]	$(HBN\text{-}tert\text{-}C_4H_9)_3$[b]
2970 s	2972 s	
2935 w	2930 m	
2895 m	2872 m	
2494 s	2520 m	2631 s
1474 s	2478 s	2560 s
1439 vs	1468 s	2480 s
1376 m	1440 vs	1600 w
1354 m	1380 m	1420 s, b
1326 m	1364 m	1360 s
1110 w	1348 m	1200 s
1088 m	1262 w	1081 s
1071 m	1220 w	1029 w
925 w	1170 m	873 s
900 w	1145 w	752 w
880 s	1130 w	740 w
791 w	1111 w	719 w
672 w	1100 w	688 w
	881 s	502 m
		472 w

[a] Neat liquid between KBr salt plates. [b] As Nujol mull between KBr salt plates.

in good agreement with literature values. The infrared spectrum of *N*-triethylborazine was reported in ref 9. Literature values for the proton magnetic resonance spectrum of *N*-triethylborazine[13] are listed in Table III for comparison with the values obtained in this study. Significantly, no other resonances except those listed in Table III and the solvent signal were observed. The mass spectrum of this material revealed a molecular ion at *m/e* 165 (the molecular weight of $(H^{11}BNC_2H_5)_3$ is 165) and a base peak at *m/e* 150 (M − 15) due to the loss of one methyl group. The molecular ion and the M − 15 fragment exhibit a typical isotopic cluster pattern expected for fragments which contain three boron atoms. A simple calculation based on the natural relative isotopic abundances for ^{10}B and ^{11}B of 19.91 and 80.09%, respectively, reveals a cluster pattern of four peaks separated by a single *m/e* unit in the ratio 1.5 (all three boron atoms ^{10}B): 18.5 ($2^{10}B + {}^{11}B$):74.5 ($^{10}B + 2^{11}B$):100% (all three boron atoms ^{11}B). The relative ratio of the observed isotopic cluster for the M − 15 fragment (relative ratio of *m/e* 147, 148, 149, and 150) was 3.2:25.0:73.5:100.0.

Reaction of Isopropylamine, Phenyl Borate, Aluminum, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), isopropylamine (0.1 mol, 8.55 ml), phenyl borate (30 g, 0.1 mol), and benzene (100 ml) were heated at 150° under 3000 psig of hydrogen for 12 hr (reaction 2, Table I). The chamber was allowed to cool and was vented; the benzene-soluble material was separated from unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid of low volatility. The infrared spectrum of this material (Nujol mull) exhibited aromatic ν(C–H) (>300 cm^{-1}) and ν(B–H) (strong absorption at 2475 cm^{-1}) in addition to other normal C–C and N–C frequencies. *N*-Triisopropylborazine was collected in a Schlenk tube (cooled to −120°) by heating this material at 200° under vacuum (0.25 mm). Aluminum phenoxide remained as the residue. The borazine was purified by vacuum distillation (44° at 0.1 mm compared to the literature value[14] of 46° at 1.1 mm) and the yield was found to be 6.4 g, 93%. Purity and identity were established by infrared, proton magnetic, and mass spectral techniques. These data are compiled in Tables II–IV, respectively. The mass spectrum of this material exhibited a weak molecular ion at *m/e* 207 (mol wt of $(H^{11}BN\text{-}i\text{-}C_3H_7)_3$ 207) and a strong M − 15 fragment at *m/e* 192 (due to loss of one methyl group). The isotopic cluster pattern for the M − 15 fragment (relative intensity of *m/e* 189, 190, 191, and 192) was found to be 6:22:70.5:100.

Reaction of *tert*-Butylamine, Aluminum, Phenyl Borate, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), phenyl borate (30 g, 0.1 mol), *tert*-butylamine (10.5 ml, 0.1 mol), and benzene (100

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TABLE III
N-TRIALKYLBORAZINE NMR DATA

Compd	τ[c]	Area ratio	Multiplicity	J[c]	Assignment
$(HBNC_2H_5)_3$[a]	6.64 (6.66)	2.0	Quartet	7.0 (7.1)	*N*-C_2H_5 (methylene)
	8.90 (8.86)	3.0	Triplet	7.0 (7.1)	*N*-C_2H_5 (methyl)
$(HBN\text{-}i\text{-}C_3H_7)_3$[a]	6.13 (6.33)	1.0	Septet	7.0 (7.0)	*N*-*i*-C_3H_7 (methyne)
	8.63 (8.77)	6.0	Doublet	7.0 (6.8)	*N*-*i*-C_3H_7 (methyl)
$(HBN\text{-}tert\text{-}C_4H_9)_3$[b]	8.64 (8.63)	...	Singlet	... (...)	*N*-*tert*-C_4H_9

[a] Neat material (trace benzene as internal standard). [b] Concentrated solution in CH_2Cl_2 (CH_2Cl_2 standard). [c] Literature values are included in parentheses for comparison. Data from ref 13.

TABLE IV
MASS SPECTRAL DATA FOR *N*-TRIALKYLBORAZINES

$(HBNC_2H_5)_3$		$(HBN\text{-}i\text{-}C_3H_7)_3$		$(HBN\text{-}tert\text{-}C_4H_9)_3$	
m/e	Rel intens	*m/e*	Rel intens	*m/e*	Rel intens
165	8.9	207	1.25	249	1.29
164	11.2	192	93.7	234	100.0
163	4.9	191	66.2	233	70.5
162	2.3	190	20.6	232	10.2
150	100.0	189	5.63	231	1.29
149	73.5	165	6.25	178	42.3
148	25.0	164	7.50	177	28.6
147	3.2	150	92.6	176	5.13
93	4.5	149	70.0	100	18.0
79	6.6	148	20.0	93	25.8
78	27.4	147	4.38	92	3.84
77	10.9	79	16.3	58	88.5
63	4.9	78	100.0	57	25.8
52	9.9	77	27.5	53	1.29
51	9.2			52	2.56
50	8.2			51	1.29
39	4.3			50	1.29
38	6.0			44	25.8
37	3.3			42	25.8
				41	32.0
				39	12.8
				32	25.8
				28	60.4

ml) were heated at 120° under 3000 psi of hydrogen for 12 hr (reaction 3, Table I). The chamber was allowed to cool and was vented; the benzene-soluble material was separated from excess, unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid. The infrared spectrum of this material (Nujol mull) revealed ν(B-H) (2560 cm^{-1}), aromatic ν(C-H) (3100 cm^{-1}), weak ν(N-H) (3650 cm^{-1}), and other "fingerprint" frequencies. The weak ν(N-H) band indicates the presence of $H_nBN(H_{n-1})$-*tert*-C_4H_9 (n = 1 or 2) compounds in admixture with the expected *N*-tri-*tert*-butylborazine. This mixture was therefore heated at 200° for 2 hr to pyrolize any primary aminoborane contaminant. The infrared spectrum of the heated material did not exhibit a band in the 3650-cm^{-1} region, indicating complete pyrolysis. *N*-tri-*tert*-butylborazine was sublimed by heating the mixture at 80° (0.25 mm). It was difficult to obtain complete isolation of the borazine due presumably to its relatively low volatility under these conditions. Complete isolation required several sublimation attempts which involved mechanically "breaking up" the solid residue repeatedly in the drybox. The sublimed material obtained in these steps was combined and resublimed at 80° (0.25 mm); yield 7.15 g, 86%. The purity and identity of this product was determined by its melting point of 93° (lit.[15] mp 94°) and by infrared, proton magnetic resonance, and mass spectral analyses (Tables II–IV, respectively). The spectral data compare well with the literature values.[13,15] The mass spectrum of this solid revealed a weak molecular ion at *m/e* 249 and an intense M − 15 peak at *m/e* 234. The isotopic cluster for the M − 15 peak (relative intensities of *m/e* 231, 232, 233, and 234) was found to be 1.9:17.1:70.3:100.0.

Results and Discussion

The reaction of primary, secondary, and tertiary monoalkylamines (alkyl = ethyl, isopropyl, and *tert*-butyl) with phenyl borate, aluminum, and hydrogen (3000 psig) in benzene solution proceeds to give the corresponding *N*-trialkylborazine in high yield (82–93%) according to the equation

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \quad (7)$$

where R = C_2H_5, *i*-C_3H_7, and *tert*-C_4H_9.

The exact reaction conditions and product yields are summarized in Table I. According to this study, heating equimolar mixtures of phenyl borate and monoalkylamine with excess aluminum and hydrogen gives 82% yield of *N*-triethylborazine after 5 hr (reaction 1), 93% yield of *N*-triisopropylborazine, and 86% yield of *N*-tri-*tert*-butylborazine after 12 hr (reactions 2 and 3, respectively). The adopted procedure involves filtration of the reaction products (to remove excess, unreacted aluminum metal) followed by removal of the reaction solvent under vacuum and distillation (in the case of the ethyl and isopropyl compounds) or sublimation (in the case of the *tert*-butyl derivative) of the borazine product from by-product aluminum phenoxide. Although this by-product is normally insoluble in hydrocarbon solvents, it was found to be largely soluble in hydrocarbon solutions of a *N*-trialkylborazine.

A high-temperature digestion step was found necessary for synthesis of *N*-tri-*tert*-butylborazine prior to sublimation of this product (see Experimental Section for details) due to the presence of trace primary amine-borane impurities ($H_nBN(H_{n-1})$-*tert*-C_4H_9, n = 2 or 3) which persisted under conditions of the direct preparation reaction (120° for 12 hr). That these species are pyrolized only slowly to the borazine at these temperatures was demonstrated by direct pyrolysis of *tert*-butylamine–borane at ~100°.[15]

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[Reprinted from Inorganic Chemistry, 10, 906 (1971).]

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Synthesis and Characterization of Dialkyl(aryl)aminomagnesium Hydrides and Alkoxy(aryloxy)magnesium Hydrides[1]

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Received September 21, 1970

Dialkyl(aryl)aminomagnesium hydrides ($HMgNR_2$ where R = C_2H_5, i-C_3H_7, n-C_4H_9, C_6H_5) have been synthesized by hydrogenation of dialkyl(aryl)aminomagnesium alkyls, $LiAlH_4$ reduction of dialkyl(aryl)aminomagnesium alkyls, and KH reduction of dialkylaminomagnesium bromides. The hydrides were characterized by elemental analysis, X-ray powder diffraction, and infrared spectroscopy. Infrared absorption bands in the 1500–1600- and 650–700-cm^{-1} regions are assigned to Mg–H stretching and bending modes, respectively, by comparison with the corresponding deuterated compounds. $HMgN(n\text{-}C_4H_9)_2$ and $HMgN(C_6H_5)_2$ are soluble in tetrahydrofuran and have been found to exhibit stereoselectivity in their reduction of ketones. Alkoxy(aryloxy)magnesium hydrides (HMgOR where R = CH_3, i-C_3H_7, $tert$-C_4H_9, C_6H_5) were shown to be unstable and to disproportionate readily to MgH_2 and $Mg(OR)_2$.

Introduction

Compounds of the type HMOR and $HMNR_2$ are known[3] where M = Be, Zn, B, or Al. Conspicuous by their absence are such compounds where M = magnesium. Bauer[4] reported the formation of $HMgOC_2H_5$ by C_2H_5MgH cleavage of $(C_2H_5)_2O$ but did not give any evidence that the compound was not a mixture of MgH_2 and $Mg(OC_2H_5)_2$. Coates[3c] has briefly reported the formation of a soluble aminomagnesium hydride when MgH_2 was allowed to react with trimethylethylenediamine in toluene.

Recently we have reported on the preparation of HMgX compounds where X = Cl, Br, or I.[5] Unfortunately we found that these compounds disproportionate in ether solvents to MgH_2 and MgX_2 (eq 1).

$$2HMgX \longrightarrow MgH_2 + MgX_2 \quad (1)$$

Now we wish to report on the integrity of HMgX compounds where X = OR or NR_2. Shortly we will report on HMgX compounds where X = alkyl or aryl. Thus moving from right to left in the periodic chart, the nature of X will have been studied for HMgX compounds for halogen (group VII), oxygen (group VI), nitrogen (group V), and carbon (group IV). In addition to preparing and characterizing these compounds and studying their structure in solution, we are also interested in evaluating these classes of compounds as stereoselective reducing agents.

Experimental Section

Apparatus.—Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice–acetone traps to remove solvent.[6]

Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer. Solution spectra were obtained in a cell with KBr windows and solid spectra were obtained as Nujol mulls between CsI plates. X-Ray powder data were obtained on a Philips Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. d spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300-ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high-pressure hydrogenation. An ebullioscopic apparatus previously described was used for molecular weight determination.[7]

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Magnesium and aluminum were determined by EDTA titration.

Materials.—Methanol (Fisher Scientific) was distilled after treating with magnesium metal. *tert*-Butyl alcohol (Fisher Scientific) was fractionally crystallized under nitrogen. 2-Propanol (Fisher Scientific) was distilled after drying over Molecular Sieve 4A. Phenol (Mallinckrodt) was distilled at reduced pressure. Diethyl-, diisopropyl-, and di-n-butylamine (Eastman Organic Chemicals) were dried over Molecular Sieve 4A and distilled prior to use. Diphenylamine (Eastman Organic Chemicals) was used without further purification.

Diethyl ether was distilled immediately before use from lithium aluminum hydride, and tetrahydrofuran and benzene were distilled from sodium aluminum hydride.

A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared by stirring a diethyl ether slurry overnight followed by filtration of the slurry through dried Celite Analytical Grade Filter Aid (John-Mansville). The solution was standardized by aluminum analysis. In a similar manner a solution of lithium aluminum deuteride (Metal Hydrides Inc.) was prepared. Potassium hydride was obtained from Alfa Inorganics.

Diisopropyl- and diethylmagnesium were prepared by the dioxane precipitation method.[8] Di-*sec*-butylmagnesium was prepared from active $MgCl_2$ and *sec*-butyllithium in benzene.[9] Magnesium hydride was prepared from $LiAlH_4$ and diethylmagnesium in diethyl ether.[10] *Anal.* Calcd for MgH_2: Mg, 92.3; H, 7.65. Found: Mg, 72.9; H, 6.26; Al, 0; $(C_2H_5)_2O$, 20.8 by difference. The ratio of Mg:H is 1.00:2.07.

Alkyl(aryl)oxymagnesium alkyls[11] and dialkyl(aryl)aminomagnesium alkyls[12] were prepared according to the methods described by Coates which involve adding an equivalent amount of alcohol or secondary amine to the appropriate dialkylmagnesium compound in diethyl ether at room temperature. After 1 hr the diethyl ether solvent was removed at reduced pressure and benzene was added in order to prepare a standardized solution in a nonpolar solvent.

(1) We are indebted to the Office of Naval Research under Contract No. N00014-67-A-0159-0005 and ONR Contract Authority No. NR-92-050/12-5-67-429 for support of this work.

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TABLE I
ANALYTICAL, INFRARED, AND X-RAY POWDER DATA FOR DIALKYL(ARYL)AMINOMAGNESIUM HYDRIDES

Compound	Analyses, % Calcd	Analyses, % Found	Infrared bands, 2000–400 cm^{-1}	X-Ray powder data
$HMgN(i\text{-}C_3H_7)_2$[a]	H, 0.803 Mg, 19.37	H, 0.619 Mg, 17.76	1500 sh, 1335 w, 1315 w, 1170 w, 1150 s, 1120 m, 975 s, 935 w, 900 m, 825 w, 810 w, 780 w, 725 s, 690 s, 650 s, 570 m, 535 w, 430 w	9.5 s, 5.25 s, 4.20 vvw
$HMgN(i\text{-}C_3H_7)_2$[h]		H, 0.819 Mg, 19.56	1500 sh, 1330 w, 1315 w, 1255 w, 1170 w, 1150 s, 1120 m, 975 s, 935 w, 900 m, 825 w, 810 w, 775 m, 725 s, 690 s, 650 s, 570 s, 545 w, 420 w	9.5 s, 5.20 s, 4.00 vw
$DMgN(i\text{-}C_3H_7)_2$[i]	D, 1.587 Mg, 19.22	D, 1.432 Mg, 20.17	1330 w, 1315 w, 1255 w, 1170 w, 1150 s, 1120 m, 1050 s, b, 975 s, 935 w, 900 m, 825 w, 810 w, 775 w, 715 w, 570 s, 525 s, 465 s	...
$HMgN(i\text{-}C_3H_7)_2$[b]		H, 1.45 Mg, 26.90	1590 s, 1345 w, 1320 w, 1170 w, 1150 s, 1110 s, 1090 w, 1025 w, 975 s, 945 m, 890 s, 720 w, 655 s, 580 s, 425 s	11.5 s, 5.50 s, 4.00 m, 3.55 w, 2.80 vw, 2.15 vvw
$HMgN(n\text{-}C_4H_9)_2$[c]	H, 0.656 Mg, 15.83	H, 0.947 Mg, 18.42	1600 s, b, 1260 w, 1230 w, 1215 w, 1155 m, 1130 m, 1105 s, 1075 s, 1055 m, 1010 m, 995 w, 945 m, 915 m, 885 m, 715 s, 675 s, 565 s, 400 s	12.5 s, 4.65 s, 4.30 m, 2.85 w
$HMgN(n\text{-}C_4H_9)_2$[d]		H, 0.727 Mg, 16.91	1550 s, b, 1300 w, 1255 w, 1150 w, 1130 m, 1105 m, 1075 s, 1010 m, 955 w, 855 m, 790 m, 715 s, 650 m, 570 s, 400 w	15.0 vs, 4.40 m
$HMgN(C_2H_5)_2$[e]	H, 1.034 Mg, 24.98	H, 0.752 Mg, 20.74	1520 s, b, 1295 w, 1165 m, 1130 s, 1095 m, 1030 w, 1015 w, 990 m, 845 m, 775 w, 720 s, 670 s, 570 s, 530 s, 440 m	14.0 s, 4.50 vw
$HMgN(C_6H_5)_2$[f]	H, 0.521 Mg, 12.25	H, 0.383 Mg, 10.87	1600 m, b, 1580 s, 1480 s, 1370 m, 1360 sh, 1330 w, 1295 m, 1235 s, 1215 sh, 1170 s, 1070 w, 1020 m, 870 s, 800 m, 740 s, 680 s, 495 s, 435 w	12.0 s, 9.0 w, 7.0 w, 6.10 w, 5.00 m, 3.95 s, 3.5 w, 2.75 w, 2.06 m, 1.80 vw
$HMgN(CH_3)CH_2CH_2N(CH_3)_2$[g]	H, 0.797 Mg, 19.92	H, 1.05 Mg, 21.92	1370 m, 1340 s, 1280 m, 1245 w, 1190 w, 1165 m, 1145 s, 1105 s, 1030 s, 940 s, 845 s, 795 s, 670 w, 575 m, 400 s	9.7 s, 8.0 s, 5.50 m, 4.70 s, 4.00 w, 2.58 vw, 2.40 w

[a] Hydrogenation of *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$ at 25°. [b] Hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70°. [c] Hydrogenation of $C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50°. [d] Hydrogenation of *sec*-$C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25°. [e] Hydrogenation of *sec*-$C_4H_9MgN(C_2H_5)_2$ at 25°. [f] Hydrogenation of $C_4H_9MgN(C_6H_5)_2$ at 25°. [g] Hydrogenation of $C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ at 110°. [h] Reaction of $C_2H_5MgN(i\text{-}C_3H_7)_2$ with $LiAlH_4$. [i] Reaction of $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ with $LiAlD_4$.

Dialkyl(aryl)aminomagnesium bromides were prepared from C_2H_5MgBr and an equivalent amount of secondary amine in tetrahydrofuran at room temperature.

Preparation of $HMgNR_2$ (R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, C_6H_5). (1) **Hydrogenation of Dialkyl(aryl)aminomagnesium Compounds.**—Dialkyl(aryl)aminomagnesium alkyl solutions (0.2–0.7 *M*) in benzene (100 ml) were hydrogenated overnight at 3000 psig. The temperature of hydrogenation depended on the particular alkyl group, R in $RMgNR_2'$: 50–70° for the ethyl group and 25° for the *sec*-butyl group. Analytical and spectroscopic data of the precipitate are given in Table I. Hydrogenation was complete in the reactions performed at 50–70°. At 25° some starting compound was generally found in the filtrates.

(2) **Reaction of Dialkylaminomagnesium Alkyls with $LiAlH_4$.** (a) **$C_2H_5MgN(i\text{-}C_3H_7)_2$.**—To a diethyl ether (25 ml) solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ (38 mmol), $LiAlH_4$ (9.5 mmol) in diethyl ether was added slowly from an additional funnel. An immediate precipitate formed. Analysis of the precipitate is given in Table I. The yield of $HMgN(i\text{-}C_3H_7)_2$ is quantitative. In a similar manner $DMgN(i\text{-}C_3H_7)_2$ was prepared from $LiAlD_4$.

(b) **$C_2H_5MgN(n\text{-}C_4H_9)_2$.**—To a diethyl ether (25 ml) solution of $C_2H_5MgN(n\text{-}C_4H_9)_2$ (28 mmol), $LiAlH_4$ (7.0 mmol) in diethyl ether was added. No precipitate formed. Infrared spectral analysis indicated the formation of $HMgN(n\text{-}C_4H_9)_2$; however the addition of benzene or hexane was not effective in the separation of the reaction products.

(3) **Reactions of MgH_2 and Trimethylethylenediamine.**—A slurry of MgH_2 (10 mmol) in benzene (50 ml) was allowed to react with trimethylethylenediamine (10 mmol) for several days under refluxing conditions. The reaction still contained a solid which was isolated by filtration. The solid was identified as MgH_2 by its infrared spectrum. The weight of the solid and the magnesium content indicated an MgH_2 recovery of 4.1 mmol. The filtrate showed no hydridic activity. Evaporation of benzene from the filtrate resulted in a brown oily resin.

(4) **Reaction of $BrMgNR_2$ with KH (R = *n*-C_4H_9, C_6H_5).**—A tetrahydrofuran solution of $BrMgNR_2$, prepared by reaction of C_2H_5MgBr with R_2NH in tetrahydrofuran, was stirred at room temperature for 3 days with excess KH. After filtration, analysis of the filtrate gave a ratio of Mg:H:Br as 1.00:0.99:0 when R = C_4H_9 and 1.00:96:0 when R = C_6H_5.

(5) **Reaction of $(i\text{-}C_3H_7)_2NH$ and $(n\text{-}C_4H_9)_2NH$ with MgH_2.**—A slurry of MgH_2 (7 mmol) and $(i\text{-}C_3H_7)_2NH$ (7 mmol) in benzene (40 ml) was allowed to react for 2 days under refluxing conditions. The solid was isolated by filtration. Infrared analysis of this solid (Nujol mull) showed only bands for MgH_2. The filtrate contained no magnesium. In a similar experiment with $(n\text{-}C_4H_9)_2NH$ and MgH_2 similar results were obtained.

A slurry of MgH_2 (10.9 mmol) and $(n\text{-}C_4H_9)_2NH$ (10.9 mmol) in benzene (100 ml) was allowed to react at 200° overnight in the autoclave. The solid product was isolated and subjected to spectroscopic analysis. The infrared spectrum showed MgH_2 bands, and X-ray powder diffraction showed lines corresponding to the lines of MgH_2. The filtrate contained no magnesium. In a similar experiment with $(i\text{-}C_3H_7)_2NH$, similar results were obtained.

Reduction of Ketones with $HMgNR_2$ (R = *n*-C_4H_9, *i*-C_3H_7, C_6H_5).—To a 0.213 *M* tetrahydrofuran solution of ketone (2-methylcyclohexanone, norcamphor) (1 mmol) $HMgNR_2$ (1.5 mmol) (R = C_6H_5, *n*-C_4H_9) in tetrahydrofuran (0.80 *M*) was added. After 2 hr at 0° the reaction mixture was quenched by adding aqueous NH_4Cl. A slurry of $HMgN(i\text{-}C_3H_7)_2$ in tetrahydrofuran was used at room temperature. The alcohols were analyzed by vpc.

Attempted Preparation of HMgOR. (1) **Reaction of MgH_2 and ROH (R = CH_3, *i*-C_3H_7, *tert*-C_4H_9, C_6H_5).**—In a typical case CH_3OH (6.00 mmol) was added to a slurry of MgH_2 (6.00 mmol) in benzene (50 ml). The mixture was stirred overnight under refluxing conditions. The solid product was isolated by filtration and dried *in vacuo* at room temperature. The reaction was repeated with the other alcohols in benzene and tetrahydrofuran. Analytical and X-ray powder data are given in Table II indicating the solid product to be a physical mixture of MgH_2 and $Mg(OR_2)$. In all cases the filtrates contained no magnesium.

(2) **Hydrogenation of $C_2H_5MgO\text{-}tert\text{-}C_4H_9$.**—A 0.5 *M* benzene solution of $C_2H_5MgO\text{-}tert\text{-}C_4H_9$ (50 mmol) (prepared by reaction of $(C_2H_5)_2Mg$ and *tert*-C_4H_9OH) was allowed to react with H_2 at 110° and 3000 psi in a Magne stirrer autoclave overnight. The precipitate was isolated as above. Analytical and X-ray powder data are given in Table II. The filtrate contained 10 mg-atoms of magnesium. The ratio of Mg:H:C_2H_5 in the filtrate was 1.00:0.0:0.88.

TABLE II
ANALYTICAL AND X-RAY POWDER DATA FOR "HMgOR" COMPOUNDS

Compound	Solvent	Mg:H ratio	XR-ay powder data
MgH_2	Diethyl ether	1:2.07	3.19 s, 2.50 s, 2.25 w, 1.67 s
"$HMgOCH_3$"	Benzene	1:1.17	11.0 vs, 3.20 m, 2.50 m, 2.25 w, 1.66 w
"$HMgOCH_3$"	Tetrahydrofuran	1:1.10	11.0 vs, 3.20 m, 2.50 m, 2.25 w, 1.68 w
$(CH_3O)_2Mg$	Benzene	1:0.0	11.0 vs
"HMgO-*i*-C_3H_7"	Benzene	1:1.02	8.75 s, 4.30 m, 3.25 w, 2.50 w, 2.25 vw, 1.66 w
"HMgO-*i*-C_3H_7"	Tetrahydrofuran	1:0.78	8.75 s, 4.30 m, 3.25 w, 2.50 w, 2.25 vw, 1.68 vw
$(i\text{-}C_3H_7O)_2Mg$	Benzene	1:0.0	8.8 s, 4.30 m
"HMgO-*tert*-C_4H_9"	Benzene	1:0.80	9.0 s, 8.0 m, 4.50 m, 4.30 m, 4.00 vvw, 3.45 w, 3.25 vw, 3.10 vw, 2.50 vw, 1.68 vw
"$HMgOC_4H_9$"	Tetrahydrofuran	1:0.94	9.0 s, 8.0 m, 4.50 m, 4.30 m, 4.00 w, 3.45 w, 3.25 vw, 3.05 w, 2.50 w, 2.25 vw, 1.67 w
"$HMgOC_4H_9$"[a]	Benzene	1:0.80	9.2 s, 8.5 m, 4.53 m, 4.30 m, 3.50 w, 3.20 m, 2.50 m, 2.25 w, 1.67 w
"$HMgOC_4N_9$"[b]	Benzene	1:0.60	8.8 s, 7.9 m, 4.45 m, 4.23 w, 4.00 vw, 3.45 m, 3.25 w, 3.05 w
$(tert\text{-}C_4H_9O)_2Mg$	Benzene	1:0.0	9.0 s, 8.0 s, 4.50 m, 4.30 m, 4.00 w, 3.50 m, 3.05 w
"$HMgOC_6H_5$"	Benzene	1:0.99	13.5 s, 8.5 m, 5.05 m, 4.60 vw, 4.25 s, 3.25 s, 2.50 w, 2.25 vw, 1.68 w
$(C_6H_5O)_2Mg$	Benzene	1:0.0	10.5 s, 8.5 w, 5.10 m, 4.60 w, 4.25 s, 3.25 m
"$HMgOC_6H_5$"	Tetrahydrofuran	1:1.05	10.5 s, 8.25 m, 6.90 w, 5.90 vvw, 4.85 w, 4.70 w, 4.48 m, 4.35 m, 4.15 m, 3.90 m, 3.75 m, 3.55 w, 3.45 m, 3.30 w, 3.20 w, 3.08 vw, 3.02 vw, 3.00 vw, 2.50 w, 2.40 w, 2.25 vw, 1.87 vw, 1.68 vw
$(C_6H_5O)_2Mg$	Tetrahydrofuran	1:0.0	10.5 s, 8.25 s, 6.95 s, 5.95 w, 5.15 w, 5.40 w, 5.15 w, 4.50 s, 4.35 s, 4.15 m, 3.90 s, 3.80 s, 3.65 w, 3.45 m, 3.30 w, 3.20 w, 3.00 w, 2.90 w, 2.80 w, 2.70 w, 2.40 w, 2.25 w, 1.86 w

[a] Hydrogenation of C_2H_5MgO-*tert*-C_4H_9 at 110° and 3000 psig. [b] Hydrogenation of *i*-C_3H_7MgO-*tert*-C_4H_9 at 50° and 3000 psig.

(3) Hydrogenation of *i*-C_3H_7MgO-*tert*-C_4H_9.—A 0.3 *M* benzene solution of *i*-C_3H_7MgO-*tert*-C_4H_9 (30 mmol) was hydrogenated at room temperature and 3000 psig overnight. No reaction occurred. The hydrogenation was repeated at 50° and 3000 psi overnight. A precipitate formed which was isolated as above. Analytical and X-ray powder data are given in Table II. The filtrate contained 1.0 mg-atom of magnesium and no hydridic hydrogen.

Preparation of $Mg(OR)_2$ (R = CH_3, *i*-C_3H_7, *tert*-C_4H_9, C_6H_5).—In a typical case CH_3OH (8.00 mmol) was added to a slurry of MgH_2 (4.00 mmol) in benzene. After refluxing overnight the solid was isolated by filtration. The reaction was repeated with the other alcohols in benzene and tetrahydrofuran. Analytical and X-ray powder data are given in Table II. In all cases the filtrates contained no magnesium.

Results and Discussion

The results of this study show that heretofore unknown dialkyl- and diarylaminomagnesium hydrides ($HMgNR_2$) can be successfully prepared by three different methods. The first method involves the hydrogenation of dialkyl- or diarylaminomagnesium alkyls ($RMgNR'_2$). This method was suggested by the recent report that the formation of an Mg–H bond takes place readily by hydrogenation of a magnesium alkyl compound especially when the alkyl group is *sec*-butyl.[13]

(13) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

In this manner *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$ was allowed to react with H_2 at 25° and 3000 psi to form the white solid $HMgN(i\text{-}C_3H_7)_2$ (I) (see eq 2 and 3). Compound I had

$$(sec\text{-}C_4H_9)_2Mg + HN(i\text{-}C_3H_7)_2 \longrightarrow sec\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2 + C_4H_{10} \quad (2)$$

$$sec\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2 \xrightarrow{H_2} HMgN(i\text{-}C_3H_7)_2 + C_4H_{10} \quad (3)$$

an Mg:H ratio of 1.00:0.84 and a unique X-ray powder pattern which contained no lines typical of MgH_2. The most interesting feature of the infrared spectrum (Nujol mull) (Figure 1) of I was a strong broad band at 1500

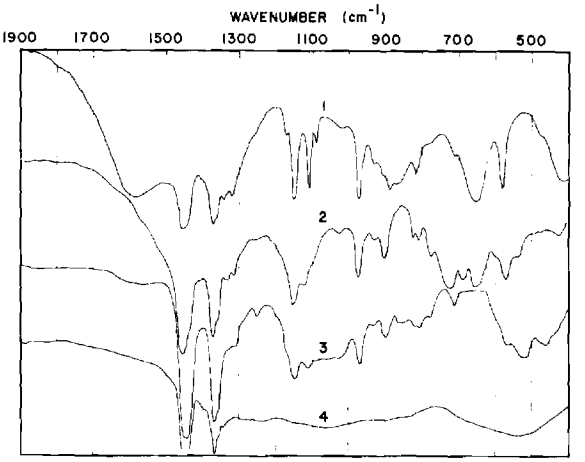


Figure 1.—Infrared spectra (Nujol mulls) of (1) $HMgN(i\text{-}C_3H_7)_2$ prepared by hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ in benzene at 70°, (2) $HMgN(i\text{-}C_3H_7)_2$ prepared by hydrogenation of *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$ in benzene at 25°, (3) $DMgN(i\text{-}C_3H_7)_2$ prepared by $LiAlD_4$ reduction of $C_2H_5MgN(i\text{-}C_3H_7)_2$ in diethyl ether, and (4) MgH_2 prepared from $LiAlH_4$ and $(C_2H_5)_2Mg$ in diethyl ether.

cm^{-1} appearing as a shoulder on the Nujol band at 1455 cm^{-1}. The assignment of this band is discussed below. Compound I is insoluble in benzene and diethyl ether and only slightly soluble in tetrahydrofuran (0.021 *M*). The molar ratio of Mg:H in the tetrahydrofuran solution was 1.00:0.98.

Adding a diethyl ether solution of $LiAlH_4$ to an ether solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ also produces I. This method is suggested by the previously reported observation that $LiAlH_4$ will reduce $(C_2H_5)_2Mg$ quantitatively to MgH_2[10] (see eq 4). On addition of $LiAlH_4$ an imme-

$$LiAlH_4 + 4C_2H_5MgN(i\text{-}C_3H_7)_2 \longrightarrow 4HMgN(i\text{-}C_3H_7)_2 + LiAl(C_2H_5)_4 \quad (4)$$

diate precipitate formed which after filtration could be completely desolvated *in vacuo* at room temperature. The X-ray powder pattern and infrared spectrum (Table I) were the same as for I prepared by hydrogenation of *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$.

In order to assign the infrared bands for the Mg–H stretching and bending modes, $DMgN(i\text{-}C_3H_7)_2$ (II) was prepared by reaction of $C_2H_5Mg(i\text{-}C_3H_7)_2$ with $LiAlD_4$. The infrared spectrum of II (Figure 1) revealed that the bands present in I at 1500, 690, and 650 cm^{-1} were absent in II and that broad bands were present in the spectrum of II at 1050 and 465 cm^{-1} approximately as predicted for the isotopic shift of Mg–H to Mg–D. The bands at 690 and 650 cm^{-1} are in the region expected for metal–hydrogen bending modes. The band at 1500 cm^{-1} is probably a terminal Mg–H stretching band;

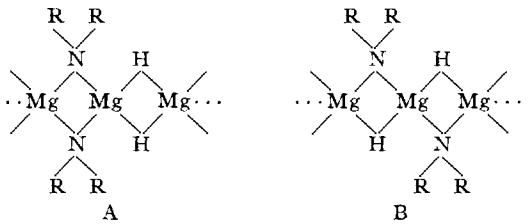
however, in a mixture of MgH_2 and $HMgN(i\text{-}C_3H_7)_2$ as discussed below, the absorption occurs at 1590 cm^{-1} and thus in I there may be some slight bridging interaction of the Mg–H bonds with adjacent molecules. This is the first time that distinct infrared absorption bands have been reported for an Mg–H compound. Reference to Figure 1 shows the characteristic Mg–H bands observed for $HMgN(i\text{-}C_3H_7)_2$ as compared to MgH_2. An Mg–H stretching frequency of 1497 and 1598 cm^{-1} for the $^2\Sigma$ and $^2\Pi$ states, respectively, has been calculated from the vapor-phase electronic emission spectra of Mg–H.[14] In a similar type of compound $HZnN(CH_3)CH_2CH_2N(CH_3)_2$, an infrared band at 1825 cm^{-1} has been reported.[3c]

Because of the low solubility of I no molecular weight determination or nmr studies were possible.

An attempt to prepare I by hydrogenation of a benzene solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70° resulted in the formation of a compound with a different X-ray powder pattern (Table I). The Mg–H infrared bands were very broad and strong at 1590 and 655 cm^{-1} (Figure 1). The Mg:H molar ratio was 1.00:1.30 which could be due to some hydrogenation of the Mg–N bond to form MgH_2, although no MgH_2 lines were visible in the X-ray powder pattern. In this connection, the hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 110° resulted in complete hydrogenation of the Mg–N bond as well as the Mg–C bond to form MgH_2 exclusively (eq 5). The fate of the amine was not determined though diisopropylamine was expected.

$$C_2H_5MgN(i\text{-}C_3H_7)_2 \xrightarrow[110°]{H_2} MgH_2 + C_2H_6 + HN(i\text{-}C_3H_7)_2 \quad (5)$$

Di-*n*-butylaminomagnesium hydride, $HMgN(n\text{-}C_4H_9)_2$ (III), was synthesized by hydrogenation of $sec\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25° and 3000 psig. The infrared spectrum of III (Nujol mull) shows strong bands at 1550 and 650 cm^{-1}, and the X-ray powder pattern contains no lines for MgH_2. Compound III is slightly soluble in benzene (0.09 *M*) and very soluble in tetrahydrofuran. When III is dissolved in tetrahydrofuran, the solution infrared spectrum shows no Mg–H stretching band at 1550 cm^{-1}. The disappearance of the band at 1550 cm^{-1} is probably due to the association of III by metal–hydrogen bridge bonds, which cause the absorption to be broadened and shifted to lower energy and thus not observable. Molecular weight data for III in tetrahydrofuran indicate that III is highly associated. The association is concentration dependent: i = 4.7 and 10 at 0.07 and 0.33 *m* concentrations, respectively. In tetrahydrofuran solution III must be associating by both the hydrido and the amino groups as would be expected by the well-known bridging tendencies of both groups. It is proposed that the association takes place *via* a double-nitrogen and double-hydrogen bridged representation (A); however mixed nitrogen–hydrogen bridge species are also possible (B) (R = *n*-C_4H_9). The association values were obtained ebullioscopically and are thought to be fairly reliable even though some solvent cleavage occurs during the determination. Over a 24-hr period in refluxing tetrahydrofuran, III decreases in hydridic hydrogen content by 50%. However, since the association measurement was done in less than 3 hr the cleavage should not be too significant.



Hydrogenation of $C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50° in benzene also produced $HMgN(n\text{-}C_4H_9)_2$, which however was of a different crystalline form (Table I). The Mg:H ratio of the product was 1.00:1.24 indicating that some hydrogenation of the Mg–N occurred. The Mg–H infrared bands occur at 1600 and 675 cm^{-1} (Nujol mull).

An attempt to prepare III by $LiAlH_4$ reduction of $C_2H_5MgN(n\text{-}C_4H_9)_2$ in diethyl ether (eq 6) was unsuccessful because both of the products of this reaction are soluble and could not be separated. The infrared spectrum of the reaction mixture shows that the expected products were formed. No Al–H bands were observed in the 1600–1700-cm^{-1} region of the spectrum, but an Mg–H band at 1500 cm^{-1} was observed. Compound III prepared in benzene by hydrogenation of $sec\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ has very slight solubility in diethyl ether, but when formed in diethyl ether, it does not precipitate. Presumably III prepared in diethyl ether is an etherate which is soluble, but the stability of the desolvated crystalline lattice is such that resolvation does not occur. Presumably this method of preparing $HMgNR_2$ compounds is successful only when the $HMgNR_2$ compound is insoluble in diethyl ether and thus easily separated from the soluble by-product $LiAlR_4$.

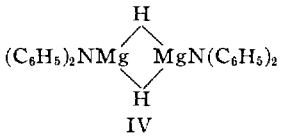
$$4C_2H_5MgN(n\text{-}C_4H_9)_2 + LiAlH_4 \longrightarrow 4HMgN(n\text{-}C_4H_9)_2 + LiAl(C_2H_5)_4 \quad (6)$$

Another route to III involves the reduction of $BrMgN(n\text{-}C_4H_9)_2$ by KH in tetrahydrofuran (eq 7). This reaction is complete in 3 days and represents the most convenient route to solutions of III in tetrahydrofuran.

$$KG + BrMgN(n\text{-}C_4H_9)_2 \longrightarrow HMgN(n\text{-}C_4H_9)_2 \quad (7)$$

Diphenylaminomagnesium hydride (IV) was synthesized by the hydrogenation of $sec\text{-}C_4H_9MgN(C_6H_5)_2$ in benzene. However, tetrahydrofuran solutions of IV can be most conveniently prepared by the KH reduction of $BrMgN(C_6H_5)_2$ in tetrahydrofuran. The Mg–H infrared stretching band (Nujol mull) occurs at about 1600 cm^{-1} largely hidden by the absorption of the phenyl groups. In a tetrahydrofuran solution spectrum with the phenyl groups and solvent absorptions, no Mg–H band is observable. Compound IV is only slightly soluble in benzene but is soluble in tetrahydrofuran (1 *M*). Colorless needle-shaped crystals are formed from a saturated solution of IV in tetrahydrofuran. Ebullioscopic molecular weight data indicate that IV is a dimer in tetrahydrofuran: i = 1.88 and 1.92 at 0.106 and 0.168 *m* concentrations, respectively. Again, however, because of solvent cleavage these association values must be viewed with caution. The hydridic hydrogen in solution decreased from an Mg:H ratio of 1.00:0.96 to a ratio of 1.00:0.81 during the measurement. In contrast to III when bridging apparently occurs with both hydrido and amino groups, the bridging in IV must be with only one group, although it is

not obvious which group is the bridging group. Although the NR_2 group is normally a stronger bridging group than hydrogen, in the case of IV the opposite may be true because of steric factors or because of the lower basicity of the diphenylamino group. If $HMgN(C_6H_5)_2$ did bridge through the diphenylamino groups, then it is not clear why further bridging through hydrogen bridge bonds does not take place as in the case proposed for $HMgN(n\text{-}C_4H_9)_2$. Thus the representation of IV as dimerizing through hydrogen bridge bonds appears as reasonable in the absence of X-ray structure data as dimerization through diphenylamino groups. For clarity in the representation of IV no solvent molecules are included; however, each magnesium is thought to be coordinated with at least one tetrahydrofuran molecule.



IV

Diethylaminomagnesium hydride, $HMgN(C_2H_5)_2$, was synthesized by hydrogenation of *sec*-$C_4H_9MgN(C_2H_5)_2$ (Table I). The compound $HMgN(C_2H_5)_2$ is insoluble in benzene and only slightly soluble in tetrahydrofuran (0.08 *M*).

Trimethylethylenediaminomagnesium hydride, $HMgN(CH_3)CH_2CH_2N(CH_3)_2$ (V), was synthesized by the hydrogenation of $C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ in benzene (Table I). Compound V is slightly soluble in benzene (0.13 *M*) and is unstable in refluxing benzene over a period of several days. An attempt to purify a sample by Soxhlet extraction resulted in loss of hydridic activity. An attempt was made to prepare V by the direct reaction of trimethylethylenediamine and MgH_2 reported earlier by Coates.[3c] No reaction occurred at room temperature; however, under conditions of atmospheric reflux for several days approximately half of the MgH_2 reacted. No hydridic activity was found in solution presumably because of the thermal decomposition of the hydride. The thermal decomposition may proceed by a hydride attack on the aminomethyl groups. Evaporation of the solvent gave a brown oily resin.

MgH_2 and diisopropyl- or di-*n*-butylamine did not react even under forcing conditions to form $HMgNR_2$ compounds (eq 8). In all cases unreacted MgH_2 was recovered.

$$MgH_2 + R_2NH \not\longrightarrow HMgNR_2 + H_2 \qquad (8)$$

No attempt was made to prepare dimethylaminomagnesium hydride because the intermediate required for hydrogenolysis, $RMgN(CH_3)_2$, is unstable and disproportionates to R_2Mg and $(CH_3)_2Mg$.[12]

The reduction of two ketones was studied in order to evaluate $HMgNR_2$ compounds as stereoselective reducing agents. The ketones are norcamphor and 2-methylcyclohexanone. Norcamphor with $HMgN(n\text{-}C_4H_9)_2$ gave 97% endo alcohol and with $HMgN(C_6H_5)_2$ 94% endo alcohol in approximately 80% yield under the conditions used, 0° and 2 hr. The endo alcohol is the expected product if the reducing agent approaches the substrate from the least hindered side of the ketone. $LiAlH_4$ under similar conditions gives 89% of the endo alcohol.[15] 2-Methylcyclohexanone with $HMgN(n\text{-}C_4H_9)_2$ gave 72% cis alcohol and with $HMgN(C_6H_5)_2$ 80% cis alcohol in 55% yield under the conditions used. The cis alcohol is the least stable alcohol. $LiAlH_4$ gives only 24% cis alcohol under similar conditions.[15] A slurry of $HMgN(i\text{-}C_3H_7)_2$ in tetrahydrofuran was used at room temperature. With 2-methylcyclohexanone $HMgN(i\text{-}C_3H_7)_2$ gave 71% cis alcohol. These results indicate that the reducing agents are attacking the substrates from the least hindered side which is consistent with the association data which indicated $HMgN(n\text{-}C_4H_9)_2$ to be highly associated and $HMgN(C_6H_5)_2$ to be at least a dimer.

In contrast to the stable aminomagnesium hydrides, the alkoxymagnesium hydrides are unstable and disproportionate to MgH_2 and magnesium alkoxide (eq 9).

$$2HMgOR \longrightarrow MgH_2 + Mg(OR)_2 \qquad (9)$$

The X-ray powder patterns (Table II) for "HMgOR" (R = CH_3, *i*-C_4H_7, *tert*-C_4H_9, C_6H_5) all show lines of MgH_2, and, in addition, the remaining lines are those of the appropriate $(RO)_2Mg$ also listed in Table II.

The synthesis of HMgOR compounds was attempted by two methods, direct reaction of MgH_2 and ROH and hydrogenation of alkylmagnesium alkoxides (RMgOR). Although the MgH_2 used was an active form prepared by $LiAlH_4$ reduction of $(C_2H_5)_2Mg$ in diethyl ether, the direct reaction with alcohols was slow and proceeded only under refluxing conditions in tetrahydrofuran or benzene. Apparently the reaction formed the intermediate "HMgOR" compound which then disproportionated to MgH_2 and $(RO)_2Mg$ (eq 10). Hydrogenation of $C_2H_5MgO\text{-}tert\text{-}C_4H_9$ at 110° in benzene resulted in the formation of a mixture of MgH_2 and $Mg(O\text{-}tert\text{-}C_4H_9)_2$ (Table II). Since disproportionation might have occurred at the higher temperature, it was considered desirable to attempt to synthesize the compound at a lower temperature. *i*-$C_3H_7MgO\text{-}tert\text{-}C_4H_9$ was synthesized and hydrogenated at room temperature. No reaction occurred at room temperature, and the hydrogenation was repeated at 50°. A product was isolated and shown to be a mixture of MgH_2 and $Mg(O\text{-}tert\text{-}C_4H_9)_2$ by X-ray powder diffraction comparison with an authentic sample.

$$MgH_2 + ROH \longrightarrow HMgOR + H_2 \longrightarrow 0.5MgH_2 + 0.5Mg(OR)_2 \qquad (10)$$

All magnesium alkoxides $(Mg(OR)_2)$ were synthesized by the reaction of MgH_2 with 2 equiv of the appropriate alcohol. All of the magnesium alkoxides are insoluble in the solvents used, benzene and tetrahydrofuran. The phenol case is somewhat complicated by the formation of different crystalline forms from different solvents.

The infrared spectra of "HMgOR" and $Mg(OR)_2$ compounds are identical. In the case of "HMgOR," the very broad weak bands of MgH_2 are not evident in the spectra. However, in no case was there any indication of Mg–H bands similar to the Mg–H bands found for the amino compounds.

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[Reprinted from Inorganic Chemistry, 10, 1888 (1971).]

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The Reaction of Lithium Aluminum Hydride with Secondary Amines in Diethyl Ether

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Received February 10, 1971

The reaction of $LiAlH_4$ with secondary amines has been studied in detail. The following compounds are formed at various stages of the reaction: Li_3AlH_6, $LiAl_2H_6NR_2$, $(R_2N)_2AlH$, $LiAlH(NR_2)_3$, and $LiAl(NR_2)_4$. The compound $LiAl_2H_6N(C_2H_5)_2$ was characterized by elemental analysis, infrared spectroscopy, and molecular association studies. A new crystalline modification of Li_3AlH_6 has been observed, and the infrared spectrum of Li_3AlH_6, prepared by the reaction of *n*-butyllithium with $LiAlH_4$, was found to be different from that previously reported.

Introduction

In their characterization of $LiAlH_4$, Schlesinger's group reported in 1947 that secondary amines react with $LiAlH_4$ to produce $LiAl(NR_2)_4$.[2] The reaction products were deduced from gas evolution studies of reaction mixtures. In 1948, in a study using $LiAlH_4$ for the measurement of active hydrogen from a series

(1) To whom all inquiries should be sent.

(2) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

of compounds, di-*n*-amylamine was found to react extremely slowly to produce 1 mol of active hydrogen.[3] The reaction products were not characterized. Recently we have reported a detailed study concerning the reaction of tertiary amines with alkali metal hydrides.[4] Because of the unusual results uncovered in this study, it seemed of interest to investigate the reaction of secondary amines with $LiAlH_4$ in diethyl ether in more detail.

Experimental Section

Apparatus.—Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide to remove oxygen and Dry Ice–acetone traps to remove solvent.[5]

Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer. Solution spectra were obtained in a cell with KBr windows and solid spectra were obtained as Nujol mulls between CsI plates. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed for 6 hr. Interplanar spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. An ebullioscopic apparatus previously described was used for molecular association determinations.[6]

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Aluminum was determined by EDTA titration. Nitrogen was determined by separating the amine from a hydrolyzed sample by distillation and titrating with standard acid potentiometrically. Lithium was determined by flame photometry.

Materials.—Piperidine and diethyl- and diisopropylamine (Eastman Organic Chemicals) were dried over Molecular Sieve 4A and distilled prior to use. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared by stirring a diethyl ether slurry overnight followed by filtration of the slurry through dried Celite Analytical Grade Filter Air (Johns-Manville). The resulting clear solution was standardized by aluminum analysis.

Diethylaminoalane[7] was synthesized by allowing $AlH_3N(CH_3)_3$ and 1 equiv of $(C_2H_5)_2NH$ to react in benzene. After the reaction was complete, the $(CH_3)_3N$ and benzene were removed at reduced pressure and diethyl ether was added. The infrared spectrum of the resulting solution in diethyl ether showed an Al–H stretching band at 1832 cm^{-1}.

Reaction of Dialkylamines with $LiAlH_4$ in Diethyl Ether. (1) **Diethylamine.**—Diethylamine, diluted in 80 ml of diethyl ether, was added gradually to $LiAlH_4$ (20.6 mmol) in diethyl ether (100 ml). Vigorous gas evolution resulted on addition of the amine and a white precipitate immediately formed. Infrared spectra were obtained on the supernatant solution at various ratios of reactants. These spectra are shown in Figure 1. The final spectrum was obtained on the clear solution that resulted when the reaction was stirred overnight.

(2) **Piperidine.**—Piperidine diluted in diethyl ether was added in increments to a diethyl ether solution of $LiAlH_4$. The observations and infrared spectra were essentially identical with those above except that the final spectrum taken after stirring overnight showed no bands in the Al–H region indicating complete reaction to form $LiAl(NC_5H_{11})_4$.

(3) **Diisopropylamine.**—Diisopropylamine diluted in diethyl ether was added to a diethyl ether solution of $LiAlH_4$. No gas evolution was immediately evident and no precipitate formed. After stirring overnight a bulky precipitate formed which solidified the entire solution. This reaction was not further characterized.

Preparation of $LiAl[N(C_2H_5)_2]_4$.—Diethylamine (326 mmol) in 100 ml of diethyl ether was slowly added to $LiAlH_4$ (81.6 mmol) in 100 ml of diethyl ether. The precipitate that formed initially disappeared on stirring overnight. An infrared spectrum showed an Al–H stretching band at 1720 cm^{-1}. The reaction was allowed to continue for 2 days under conditions of reflux. The diethyl ether was removed at reduced pressure. A slightly yellow viscous oil resulted. An infrared spectrum of the oil taken as a thin film showed only a very faint Al–H stretching band. *Anal.* Calcd for $LiAl[N(C_2H_5)_2]_4$: Li, 2.15; H, 0; Al, 8.37; N, 17.37. Found: Li, 2.11; H, 0; Al, 7.60; N, 14.22. Because of the very viscous nature of the compound solvent removal is difficult and not complete.

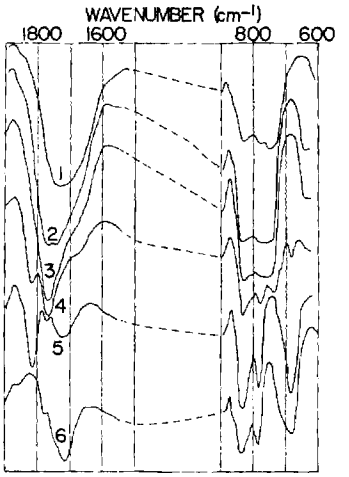

Figure 1.—Infrared spectra of the supernatant solution on adding $(C_2H_5)_2NH$ to $LiAlH_4$ in diethyl ether at the following $LiAlH_4$:$(C_2H_5)_2NH$ ratios: (1) pure $LiAlH_4$, (2) 3:1, (3) 2:1, (4) 1:1, (5) 0.5:1, and (6) 0.25:1 after stirring overnight.

Preparation of $LiAlH[N(C_2H_5)_2]_3$.—Lithium aluminum hydride (25 mmol) in diethyl ether (15 ml) was added slowly to $(C_2H_5)_2NH$ (75 mmol) in diethyl ether. A gas was evolved and a clear solution resulted. Removal of the diethyl ether solvent produced a white solid. *Anal.* Calcd for $LiAlH[N(C_2H_5)_2]_3$: Li, 2.76; Al, 12.02; H, 0.401. Found: Li, 2.95; Al, 11.15; H, 0.449.

Preparation of $LiAl_2H_6N(C_2H_5)_2$. (1) **Reaction of $LiAlH_4$ and $H_2AlN(C_2H_5)_2$.**—Lithium aluminum hydride (5.0 mmol) in diethyl ether (8 ml) was added to $H_2AlN(C_2H_5)_2$ (10.0 mmol) in diethyl ether (10 ml). The infrared spectrum of the resulting solution showed Al–H stretching bands of approximately equal intensity at 1832 and 1770 cm^{-1}. Additional $LiAlH_4$ (5.0 mmol) was added. The infrared spectrum showed only a single Al–H stretching band at 1770 cm^{-1}. Ebullioscopic association measurement gave association values of 1.09 and 1.22 at 0.071 and 0.144 *m*, respectively. Diethyl ether was removed from a portion of the sample. The desolvated sample was redissolved in diethyl ether. The sample only partially dissolved. After filtration an infrared spectrum (Nujol mull) of the solid showed broad bands characteristic of Li_3AlH_6.

(2) **Reaction of $LiAlH_4$ and $(C_2H_5)_2NH$.**—Diethylamine (16.9 mmol) in diethyl ether (25 ml) was added slowly to $LiAlH_4$ (42.3 mmol) in diethyl ether (50 ml). A gas was evolved and a white precipitate formed. After stirring overnight the solution was filtered and the solid was dried *in vacuo*. *Anal.* Calcd for Li_3AlH_6: Li, 38.66; Al, 50.0; H, 11.23. Found: Li, 36.03; Al, 47.7; H, 9.92. The amount of Li_3AlH_6 recovered was 7.2 mmol of an expected 8.6 mmol. The infrared spectrum (Nujol mull) is shown in Figure 2. The X-ray powder pattern (Table I) indicates a different crystalline modification from that previously reported.[8] In separate experiments under apparently the same conditions, Li_3AlH_6 containing the reported X-ray powder lines was obtained. An infrared spectrum of the filtrates showed only a single Al–H stretching band at 1770 cm^{-1}. Analysis of the filtrate showed an Li:Al:N:H ratio of 0.54:1.00:0.49:2.83.

Preparation of Li_3AlH_6 from *n*-C_4H_9Li and $LiAlH_4$.—Lithium aluminum hexahydride was prepared by a previously reported

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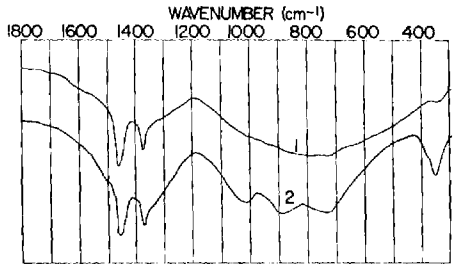

Figure 2.—Infrared spectra (Nujol mull) of Li_3AlH_6: (A) Li_3AlH_6 prepared from $LiAlH_4$ and n-C_4H_9Li, (B) Li_3AlH_6 prepared from $LiAlH_4$ and $(C_2H_5)_2NH$.

procedure.[8] The X-ray powder pattern contained the lines previously reported for Li_3AlH_6 but a few additional lines were observed (Table I). The infrared spectrum (Nujol mull) is shown in Figure 2.

TABLE I
POWDER X-RAY DIFFRACTION PATTERN OF Li_3AlH_6

n-C_4H_9Li + $LiAlH_4$				$(C_2H_5)_2NH$ + $LiAlH_4$			
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
4.94	w	1.714	w	4.88	vvw	1.641	m
4.45	m	1.642[a]	m	4.45	m	1.590	vw
4.19	w	1.592	vw	4.22	m	1.568	m
4.04[a]	vs	1.569	vw	4.07	w	1.530	w
3.93[a]	vs	1.528[a]	m	3.93	w	1.506	vvw
3.81	m	1.505[a]	m	3.81	s	1.483	vw
3.18	vw	1.483[a]	w	3.05	vw	1.403	m
2.827[a]	s	1.409[a]	m	2.823	w	1.360	vvw
2.556[a]	w	1.348[a]	w	2.694	vw	1.340	w
2.498[a]	vw	1.334[a]	w	2.439	s	1.297	vvw
2.426	m	1.315[a]	w	2.321	w	1.266	w
2.318[a]	s	1.276[a]	w	2.222	w	1.218	w
2.259[a]	m	1.250[a]	w	2.137	m	1.188	w
2.139	m	1.216[a]	w	2.051	m	1.160	w
2.051	vvw	1.159[a]	w	1.973	vw	1.087	w
2.018[a]	w	1.131	w	1.906	vvw	1.068	w
1.971[a]	w	1.121[a]	w	1.804	vw	1.047	vvw
1.799[a]	m	1.101[a]	w	1.776	vw	1.021	vvw
1.774[a]	m	1.087[a]	w	1.749	m		

[a] Previously reported for Li_3AlH_6.[8]

Results and Discussion

The addition of $(C_2H_5)_2NH$ to a diethyl ether solution of $LiAlH_4$ results in hydrogen evolution and the immediate formation of a white precipitate. The precipitate was shown to be Li_3AlH_6 by elemental analysis and comparison of the X-ray powder pattern with that of an authentic sample.[8] Infrared spectra of the supernatant solution at various ratios of $(C_2H_5)_2NH$ to $LiAlH_4$ (Figure 1) show sequentially three distinct Al–H stretching bands: 1770, 1720, and 1815 cm^{-1}. Allowing the reaction to proceed overnight at a ratio of $(C_2H_5)_2NH$ to $LiAlH_4$ of 4:1 resulted in the dissolution of the precipitated Li_3AlH_6 to form a clear solution. An infrared spectrum of the clear solution (Figure 1) showed an Al–H stretching band at 1720 cm^{-1} which is assigned to the compound $LiAlH[N(C_2H_5)_2]_3$ (eq 1).

$$LiAlH_4 + 3(C_2H_5)_2NH \longrightarrow LiAlH[N(C_2H_5)_2]_3 + 3H_2 \quad (1)$$

Only by refluxing the reaction mixture for 2 days was the completely aminated compound $LiAl[N(C_2H_5)_2]_4$ formed (eq 2). The compound $LiAl[N(C_2H_5)_2]_4$ is a

$$LiAlH_4 + 4(C_2H_5)_2NH \longrightarrow LiAl[N(C_2H_5)_2]_4 + 4H_2 \quad (2)$$

slightly yellow viscous oil. The difficulty in forming $LiAl[N(C_2H_5)_2]_4$ can be attributed to steric factors. When piperidine was used, stirring overnight was sufficient to form $LiAl(NC_5H_{11})_4$.

The compound $LiAlH[N(C_2H_5)_2]_3$ was easily prepared in diethyl ether by inverse addition of reagents. Addition of a solution of $LiAlH_4$ in diethyl ether to an ether solution of $(C_2H_5)_2NH$ results in gas evolution but no precipitation. An infrared spectrum of the solution shows the Al–H stretching band at 1720 cm^{-1}. Evaporation of the solvent resulted in a white solid which gave the correct elemental analysis for $LiAlH[N(C_2H_5)_2]_3$.

Since Li_3AlH_6 is formed in the initial stages of the reaction, the first step of the reaction must be an alane extraction reaction (eq 3) similar to that reported for tertiary amines.[4] The very reactive LiH formed then reacts with excess $LiAlH_4$ to form Li_3AlH_6 (eq 4).[8] The compound $(C_2H_5)_2NH \cdot AlH_3$ would be expected to eliminate hydrogen (eq 5) immediately forming $(C_2H_5)_2NAlH_2$.[9] The infrared spectrum of a diethyl ether solution of diethylaminoalane, $(C_2H_5)_2NAlH_2$, prepared independently, exhibited an Al–H stretching band at 1832 cm^{-1} which was not observed in the spectrum of this reaction product. Since the formation of $(C_2H_5)_2NAlH_2$ in the reaction seems likely, a further reaction between $(C_2H_5)_2NAlH_2$ and $LiAlH_4$ is proposed forming a new compound (A) $LiAl_2H_6N(C_2H_5)_2$ (eq 6). The complete reaction sequence proposed is shown below

$$2LiAlH_4 + 2(C_2H_5)_2NH \longrightarrow 2LiH + 2(C_2H_5)_2NH \cdot AlH_3 \quad (3)$$

$$2LiH + LiAlH_4 \longrightarrow Li_3AlH_6 \quad (4)$$

$$2(C_2H_5)_2NH \cdot AlH_3 \longrightarrow 2(C_2H_5)_2NAlH_2 + 2H_2 \quad (5)$$

$$2(C_2H_5)_2NAlH_2 + 2LiAlH_4 \longrightarrow 2LiAl_2H_6N(C_2H_5)_2 \quad (6)$$

$$5LiAlH_4 + 2(C_2H_5)_2NH \longrightarrow Li_3AlH_6 + 2LiAl_2H_6N(C_2H_5)_2 + 2H_2 \quad (7)$$

Equation 7 shows the overall stoichiometry of the formation of Li_3AlH_6 and compound A. A reaction carried out at this stoichiometry gave the expected amount of Li_3AlH_6 as the precipitated product and compound A was indicated by both infrared and elemental analyses.

Since the formation of $(C_2H_5)_2NAlH_2$ is proposed as an intermediate in the reaction sequence, a separate experiment was carried out involving $(C_2H_5)_2NAlH_2$ and $LiAlH_4$ in diethyl ether in order to establish the integrity of eq 6 in the reaction sequence. A diethyl ether solution of diethylaminoalane prepared independently was allowed to react with $LiAlH_4$ in 1:1 ratio. Infrared analysis of the reaction product showed no Al–H stretching band at 1740 cm^{-1} characteristic of $LiAlH_4$ but did show a strong Al–H band at 1770 cm^{-1} observed previously in the reaction described by eq 7.

Compound A does not maintain its integrity in the solid state. Evaporation of the diethyl ether solvent gave a white solid. An infrared spectrum of the solid (Nujol mull) showed a sharp band at 1832 cm^{-1} and a broad Al–H band at 1750 cm^{-1}. This spectrum suggests that compound A disproportionates to $LiAlH_4$ and $(C_2H_5)_2NAlH_2$ in the solid state

$$LiAl_2H_6N(C_2H_5)_2 \longrightarrow (C_2H_5)_2NAlH_2\downarrow + LiAlH_4\downarrow \quad (8)$$

When compound A as a solid was redissolved in diethyl ether a small portion did not dissolve. An infrared spectrum (Nujol mull) indicated that the solid was

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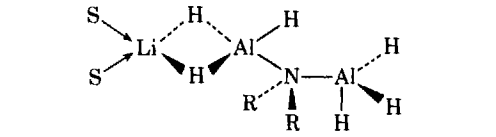
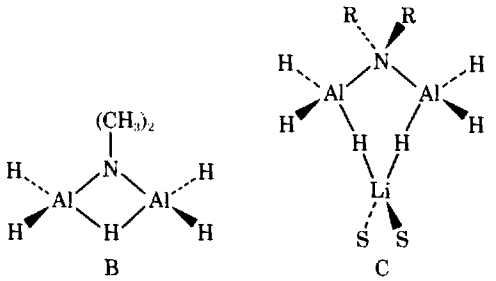
Li_3AlH_6. Infrared analysis of the solution showed, in addition to the band at 1770 cm^{-1}, an additional weak band at 1815 cm^{-1}.

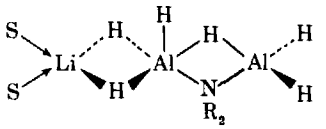
An association study indicates that compound A is a monomer at low concentrations. The structure of compound A in solution may be similar to that proposed for $(CH_3)_2NAl_2H_5$[10] (structure B); however several structures are possible (A, C, and D).



A



B C



D

Addition of $(C_2H_5)_2NH$ in excess of the $LiAlH_4$:$(C_2H_5)_2NH$ ratio of 2.5:1 results in further gas evolution and the appearance of an infrared band at 1815 cm^{-1} in the supernatant solution (Figure 1). The 1815-cm^{-1} band is observed for $[(C_2H_5)_2N]_2AlH$ prepared independently. Further addition of $(C_2H_5)_2NH$ results in the formation of a mixture of $LiAlH[N(C_2H_5)_2]_3$, $[(C_2H_5)_2N]_2AlH$, and compound A. The precipitated Li_3AlH_6 slowly reacts with additional amine until at a 1:3 $LiAlH_4$:$(C_2H_5)_2NH$ ratio the only product of the reaction is $LiAlH[N(C_2H_5)_2]_3$.

The Li_3AlH_6 formed in the extraction reaction in some instances gave an X-ray powder pattern similar to that reported for Li_3AlH_6 formed from n-C_4H_9Li and $LiAlH_4$.[8] A few additional lines were observed (Table I) even for Li_3AlH_6 prepared from n-C_4H_9Li and $LiAlH_4$. A new crystalline modification (Table I) was formed in other cases under what was thought to be identical conditions. Possibly there is very little energy difference in the two forms and minor changes in conditions result in formation of the two different forms. For a similar compound, Li_3AlF_6, three crystalline modifications have been reported.[11]

The infrared spectrum of Li_3AlH_6 prepared from n-C_4H_9Li and $LiAlH_4$ (Figure 2) shows two very broad bands centered around 700 and 1400 cm^{-1}. The infrared spectrum of Li_3AlH_6 was previously reported to show only a single absorption at 1720 cm^{-1}.[8] Since the previously reported spectrum was obtained as a KBr pellet, some hydrolysis of the compound may have occurred during the formation of the pellet. The infrared bands observed here are consistent with the bands observed for Na_3AlH_6 at 1300 and 800 cm^{-1}.[12] The infrared spectrum (Nujol mull) of Li_3AlH_6 from the reaction of $LiAlH_4$ and $(C_2H_5)_2NH$ shows splitting of the broad band at 700 cm^{-1} into three bands at 725, 885, and 1020 cm^{-1} and an additional band at 350 cm^{-1} with a possible shoulder at 370 cm^{-1}. All the Li_3AlH_6 infrared spectra from the $(C_2H_5)_2NH$ and $LiAlH_4$ reaction show some degree of splitting that is not observed with Li_3AlH_6 from n-C_4H_9Li and $LiAlH_4$ although the observed bands are very broad. However, there is no correlation between the X-ray powder data and the infrared spectra. In some cases the $(C_2H_5)_2NH$ and $LiAlH_4$ reaction produces Li_3AlH_6 with the same powder pattern as the Li_3AlH_6 from the n-C_4H_9Li and $LiAlH_4$ reaction but the infrared spectrum still shows splitting. There should be six vibrational bands for an octahedral AlH_6^{3-}[13] with only two infrared active.[13] If the shoulder on the band at 350 cm^{-1} is real or if the broad band at 1400 cm^{-1} under the Nujol bands is split, there are six bands visible in the X-ray spectrum (Figure 2) indicating that the octahedron is completely distorted allowing the forbidden bands to become active.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. N00014-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

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[Reprinted from Inorganic Chemistry, 10, 2486 (1971).]

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Preparation of New Complex Metal Hydrides. Potassium Tetrahydrozincate and Sodium Tetrahydrozincate

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Received March 1, 1971

Potassium tetrahydrozincate (K_2ZnH_4) was prepared by the reaction of KH and di-*sec*-butylzinc in benzene and tetrahydrofuran and by the hydrogenation of $KZn(sec\text{-}C_4H_9)_3$ in tetrahydrofuran. The compound K_2ZnH_4 was characterized by X-ray powder diffraction, infrared spectroscopy, elemental analysis, and dta–tga. Evidence for the existence of Na_2ZnH_4 is also presented.

Introduction

In view of our recent report[1] of the preparation of $KMgH_3$ by the hydrogenation of $KMg(sec\text{-}C_4H_9)_2H$, we wished to expand the study to include other group II metals.

Our plan was to study the reaction of KH, NaH, and LiH with a dialkylzinc compound in both hydrocarbon and ether solvent in an attempt to prepare a number of alkali metal dialkylzinc hydrides in much the same way we have prepared similar magnesium compounds. The reactions were to be carried out using di-*sec*-butylzinc, since this compound is soluble in both hydrocarbons and ethers and the *sec*-C_4H_9Zn group should be easily hydrogenolyzed to the HZn group

$$\begin{array}{ccccccc} & & MZnH_3 + 2RH & & M_2ZnH_4 + 2RH & & M_3ZnH_5 + 2RH \\ & & \uparrow H_2 & & \uparrow H_2 & & \uparrow H_2 \\ MH + R_2Zn & \longrightarrow & MZnR_2H & \xrightarrow{MH} & M_2ZnR_2H_2 & \xrightarrow{MH} & M_3ZnR_2H_3 \\ & & \downarrow R_2Zn & & & & \\ & & MZn_2R_4H & \xrightarrow{H_2} & MZn_2H_5 & & \end{array} \qquad (1)$$

where M = Li, Na, K and R = sec-C_4H_9. The italic hydrides represent new complex metal hydrides of zinc.

Shriver and coworkers have recently reported the preparation of $MZnR_2H$ compounds in ether solvent[2] and have demonstrated the existence of MZn_2R_4H compounds in solution as well (eq 2).[2] Since new complex

$$MZnR_2H + ZnR_2 \rightleftharpoons MZn_2R_4H \qquad (2)$$

metal hydrides are of considerable interest both from a structural viewpoint and as selective reducing agents in organic chemistry, we wished to synthesize the new complex metal hydrides of zinc described above.

Experimental Section

Apparatus.—Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a circulating system using manganese oxide columns to remove oxygen and Dry Ice–acetone to remove solvent.[3]

Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer as Nujol mulls between CsI plates. X-Ray powder data were obtained on a Philips Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300-ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high-pressure hydrogenation. Dta–tga data were obtained at atmospheric pressure under argon on a Mettler Thermoanalyzer 2. Alumina crucibles were used to hold the samples.

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[3] Alkali metals were determined by flame photometry. Zinc was determined by EDTA titration.

Materials.—Potassium and sodium hydrides were obtained from Alfa Inorganics as a slurry in mineral oil. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared in diethyl ether in the usual manner.

Diethyl- and di-*sec*-butylzinc were prepared by the Noller procedure.[4] Ethyl and *sec*-butyl iodides were obtained from Fisher Scientific. The iodides were dried over anhydrous $MgSO_4$ and distilled prior to use. The zinc–copper couple was obtained from Alfa Inorganics. The reactions were allowed to proceed overnight. The dialkylzinc was distilled from the reaction pot at reduced pressure. Analysis of the di-*sec*-butylzinc gave a butane to zinc ratio of 2.13:1.00.

Reaction of KH and $(sec\text{-}C_4H_9)_2Zn$ in Benzene.—Di-*sec*-butylzinc was added to a slurry of KH (34.4 mmol) in benzene previously washed with benzene to remove the mineral oil. The slurry became warm immediately and developed a slightly yellow color. A solid was always present during the reaction. The mixture was stirred overnight at room temperature. The solid was separated by filtration and dried at room temperature *in vacuo*. The resulting white solid was extremely reactive, flaming on exposure to the atmosphere. *Anal.* Calcd for K_2ZnH_4: K, 53.0; Zn, 44.3; H, 2.73. Found: K, 45.9; Zn, 37.4; H, 2.23. The molar ratio of K:Zn:H is 2.04:1.00:3.86. The amount of K_2ZnH_4 recovered was 5.5 mmol of an expected 8.6 mmol. The X-ray powder diffraction data are given in Table I. Infrared spectrum (Nujol mull) showed two strong broad bands at 500–800 cm^{-1} centered at 650 cm^{-1} and 1200–1600 cm^{-1} centered at 1400 cm^{-1}. Dta–tga showed that the sample still contained a little solvent which was lost below 80°. Thermal decomposition of the compound occurred endothermically at 242, 292, and 336°. The simultaneous weight loss curve showed inflections that corresponded to the loss of weight equivalent to one hydrogen each at the first two endotherms and to two hydrogens at the final endotherm. Analysis of the filtrate gave a ratio of K:Zn:H:C_4H_9 of 1.18:1.00:0.14:2.98. The filtrate contained 17 mmol of $KZn(sec\text{-}C_4H_9)_3$ based on zinc analysis.

Reaction of Excess KH with $(sec\text{-}C_4H_9)_2Zn$ in Tetrahydrofuran.—Di-*sec*-butylzinc (26.2 mmol) was added to a slurry of KH (59.3 mmol) in tetrahydrofuran. The KH had been previously washed with tetrahydrofuran to remove the mineral oil. The slurry became warm immediately turning slightly yellow. The mixture was stirred overnight. A solid remained throughout the

(1) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

(2) G. J. Kubas and D. F. Shriver, *ibid.*, **92**, 1949 (1970).

(3) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(4) C. R. Noller, *Org. Syn.*, **12**, 86 (1932).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR K_2ZnH_4

K_2ZnH_4[a]		K_2ZnH_4 + Zn[b]		—Zn[c]—		K_2ZnH_4 + KH[d]		—KH[e]—		—ZnH_2[f]—	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
5.10	w	5.10	w			5.05	w			4.51	vw
4.26	m	4.27	m			4.25	m			4.23	s
3.89	w	3.89	w			3.90	w			3.80	vw
3.62	vw	3.62	vw			3.60	vw			3.40	m
3.47	m	3.47	m			3.30	s	3.30	vs	2.97	vw
3.24	w	3.24	w			3.10	s			2.828	vw
3.09	s	3.08	s			2.95	s			2.608	w
2.940	s	2.941	s			2.85	s	2.86	s	2.468	vw
2.744	w	2.743	w			2.91	w			2.387	m
2.568	vvw	2.568	w			2.33	m			2.290	m
2.354	w	2.469	s	2.473	m	2.13	m			2.225	m
2.128	w	2.353	w			2.03	m	2.02	s	2.135	w
1.946	w	2.305	s	2.308	m	1.96	vw			2.085	w
1.814	w	2.128	w			1.82	vw			2.017	vw
1.734	w	2.090	vs	2.091	s	1.72	m	1.72	s	1.905	w
1.648	vw	1.945	w			1.64	w	1.65	m	1.764	w
1.624	vw	1.814	w			1.55	w			1.688	vw
1.571	w	1.734	w			1.49	vw	1.43	m	1.630	vw
1.488	w	1.681	s	1.687	m	1.39	vw	1.31	m	1.562	vw
1.470	w	1.648	vw					1.28	m	1.486	vw
1.384	vw	1.624	vw					1.17	m	1.464	vw
1.213	w	1.571	w					1.10	m	1.416	vw
		1.551	vw					1.01	w	1.336	vw
		1.487	w							1.305	vw
		1.471	vw							1.295	vw
		1.384	vw							1.259	vw
		1.340	s	1.342	m					1.219	vw
		1.330	s	1.332	m					1.172	vw
		1.236	w	1.237	w					1.157	vw
		1.213	w							1.123	vw
		1.172	w	1.173	m					1.042	vw
		1.153	s	1.154	w						
		1.123	w	1.124	w						
		1.090	m	1.091	w						
				1.046	w						

[a] KH + $(sec\text{-}C_4H_9)_2Zn$ in benzene. [b] Hydrogenation of $KZn(sec\text{-}C_4H_9)_3$. [c] ASTM file. [d] Excess KH + $(sec\text{-}C_4H_9)_2Zn$. [e] ASTM files. [f] $LiAlH_4$ + $(C_2H_5)_2Zn$.

reaction. The solid was separated by filtration and dried *in vacuo* at room temperature. Analysis showed a ratio of K:Zn:H of 3.23:1.00:4.68. X-Ray powder data are given in Table I.

Analysis of the filtrate showed a ratio of K:Zn:H:*sec*-C_4H_9 of 0.96:1.00:0.26:2.87. The filtrate was subjected to hydrogenation at 3000 psi and 40° for 24 hr. A black precipitate was recovered from the autoclave. X-Ray powder pattern is shown in Table I.

Reaction of NaH and $(sec\text{-}C_4H_9)_2Zn$ in Benzene.—Di-*sec*-butylzinc (31.9 mmol) was added to a slurry of NaH (42.6 mmol) in benzene. The NaH had been previously washed with benzene to remove the mineral oil. No immediate reaction was obvious. After stirring 1 week, analysis of the supernatant showed a Zn:*sec*-C_4H_9 ratio of 1:2.09 with no hydridic hydrogen.

Reaction of NaH and $(sec\text{-}C_4H_9)_2Zn$ in Dimethoxyethane.—Di-*sec*-butylzinc (16.7 mmol) was added to a slurry of NaH (excess) in dimethoxyethane. Analysis of the supernatant after stirring for 1 week showed a zinc:hydride ratio of 2:1. The mixture was filtered and the filtrate subjected to hydrogenation at 3000 psig and 40° for 2 hr. A black precipitate was isolated from the autoclave. X-ray powder diffraction pattern is shown in Table II. Dta-tga spectrum of the precipitate showed weak endotherms at 190, 220, and 265° with a corresponding continuous weight loss and a strong endotherm at 322° with no weight loss.

Attempt to Prepare ZnH_2 by Hydrogenation of $(sec\text{-}C_4H_9)_2Zn$ in Benzene.—A benzene (100 ml) solution of $(sec\text{-}C_4H_9)_2Zn$ (35.4 mmol) was hydrogenated overnight at 3000 psi at room temperature. No reaction occurred. The hydrogenation was repeated at 50°. A black precipitate resulted which was shown to be elemental zinc by X-ray powder diffraction.

Preparation of ZnH_2 by $LiAlH_4$ Reduction of $(sec\text{-}C_4H_9)_2Zn$.—Lithium aluminum hydride (14.1 mmol) in diethyl ether (30 ml) was slowly added to diethylzinc (9.4 mmol) in diethyl ether (25 ml). The reaction was allowed to stir overnight at room temperature and the precipitate isolated by filtration. *Anal.* Calcd for ZnH_2: Zn, 97.0; H, 2.99. Found: Zn, 87.2, H, 2.69. The X-ray powder pattern is shown in Table I. Dta-tga spectrum of ZnH_2 showed a very rapid exothermic *decomposition at 85°*.[5]

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR Na_2ZnH_4

—Na_2ZnH_4 + Zn[a]—		—Zn[b]—		—K_2ZnH_4[c]—	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
5.082	m			5.10	w
4.80	vw			4.26	m
4.04	m				
3.92	m			3.89	w
3.36	m			3.62	vw
3.07	w			3.47	m
2.921	w			3.24	w
2.751	s			3.09	s
2.585	w			2.940	s
2.468	s	2.473	m	2.744	w
2.373	m			2.568	vvw
2.306	s	2.308	m	2.354	w
2.156	w			2.128	w
2.087	vs	2.091	s		
1.964	vw			1.946	w
1.941	vw				
1.812	vw			1.814	w
1.749	vw				
1.683	s	1.687	m	1.734	w
1.644	vw			1.648	vw
1.596	vw			1.624	vw
1.553	vw			1.571	w
1.478	vw				
1.378	vvw			1.488	w
1.339	s	1.342	m	1.470	w
1.330	s	1.332	m	1.384	vw
1.236	vw	1.237	w	1.213	w
1.172	s	1.173	m		
1.149	w	1.154	w		
1.123	s	1 124	m		
		1.090	w		
		1.046	w		

[a] Hydrogenation of $NaH[(sec\text{-}C_4H_9)_2Zn]_2$. [b] ASTM files. [c] $KH(sec\text{-}C_4H_9)_2Zn$.

Results and Discussion

Contrary to the reaction of dialkylzinc compounds with NaH and LiH to form R_2Zn–MH complexes in ether solvents,[2] KH and di-*sec*-butylzinc were found to react directly to form a new hydride, K_2ZnH_4, both in hydrocarbon and ether solvent

$$4KH + 3R_2Zn \longrightarrow K_2ZnH_4 + 2KZnR_3 \quad (R = sec\text{-}C_4H_9) \quad (3)$$

The reaction is relatively rapid and the isolation of an intermediate R_2Zn–KH complex was not possible. The X-ray powder pattern of K_2ZnH_4 contained no lines for KH or ZnH_2 (Table I). When a reaction with excess KH was carried out, the X-ray powder diffraction pattern showed lines for KH in addition to the lines for K_2ZnH_4 (Table I). Zinc hydride was prepared by the reaction of $LiAlH_4$ and $(C_2H_5)_2Zn$ in diethyl ether after an attempt to prepare it by the hydrogenation of $(sec\text{-}C_4H_9)_2Zn$ failed. The X-ray powder pattern of ZnH_2 is included in Table I.

Since no complex of KH and dialkylzinc could be isolated for hydrogenation, an attempt was made to prepare $KZnH_3$ by the hydrogenation of $KZn(sec\text{-}C_4H_9)_3$ in tetrahydrofuran. The hydrogenation (eq 4) produced a black precipitate which was shown by X-ray powder pattern to be a mixture of K_2ZnH_4 and elemental zinc (Table I). Apparently K_2ZnH_4 is the most

$$2KZn(sec\text{-}C_4H_9)_3 + 3H_2 \longrightarrow K_2ZnH_4 + Zn + 6C_4H_{10} \quad (4)$$

stable complex potassium zinc hydride.

In contrast to ZnH_2 which decomposes slowly at room temperature and rapidly at 85°, K_2ZnH_4 is very ther-

(5) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartick, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 4585 (1951).

mally stable. Dta–tga analysis shows endotherms during decomposition at 242, 292, and 336°.

The infrared spectrum (Nujol mull) of K_2ZnH_4 shows two strong broad bands at 1400 and 650 cm^{-1}. These bands are consistent with octahedral coordinated zinc, since in the related system of magnesium hydrides (MgH_2 and $KMgH_3$) where the magnesium is known to be octahedrally coordinated, broad infrared bands occur at 1160 and 650 cm^{-1}.[6]

Although we have not indexed the powder pattern, the most likely structure of K_2ZnH_4 would seem to be that of K_2ZnF_4[7] which is the K_2NiF_4[8] structure.

We observed that NaH and di-*sec*-butylzinc do not react in hydrocarbon; however a 1:2 complex of NaH: (*sec*-$C_4H_9)_2Zn$ [$NaZn_2R_4H$] was formed in dimethoxyethane. Although NaH was used in excess, a 1:1 ($NaZnR_2H$) or 2:1 ($Na_2ZnR_2H_2$) complex was not observed. Hydrogenation of this complex produced a black solid. The X-ray powder diffraction pattern (Table II) indicated that the solid was a mixture of zinc metal and another compound with a similar pattern to K_2ZnH_4, probably Na_2ZnH_4. When the black solid was subjected to dta–tga, a decomposition pattern similar to that observed for K_2ZnH_4 was obtained. The stepwise endothermic decomposition occurs at slightly lower temperatures: 190, 220, and 265°. A fourth endotherm is observed at 322° with no weight loss that is associated with the melting of zinc metal. On the basis of the X-ray powder pattern and the dta–tga, the existence of Na_2ZnH_4 seems likely.

An attempt to prepare $LiZnH_3$ or Li_2ZnH_4 by hydrogenolysis of the reaction production of *sec*-C_4H_9Li and (*sec*-$C_4H_9)_2Zn$ in benzene solvent was not successful. Instead, a solid product was produced which exhibited an X-ray powder pattern characteristic of LiH. It was hoped that reaction of Li-*sec*-C_4H_9 and Zn(*sec*-$C_4H_9)_2$ would take place to produce $LiZn$(*sec*-$C_4H_9)_3$ which then would be hydrogenalyzed to form either $LiZnH_3$ or Li_2ZnH_4

$$\text{Li-}sec\text{-}C_4H_9 + (sec\text{-}C_4H_9)_2Zn \longrightarrow LiZn(sec\text{-}C_4H_9)_3 \xrightarrow{H_2} LiZnH_3 \text{ or } Li_2ZnH_4 \quad (5)$$

Work is in progress to prepare other complex metal hydrides of zinc.

Acknowledgment.—We are indebted to the Office of Naval Research (Grant NOO14-67-A-0159-0005) for support of this work.

(6) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

(7) O. Schmitz-Dumont and H. Bornefeld, *Z. Anorg. Allg. Chem.*, **287**, 120 (1956).

(8) D. Balz and K. Plieth, *Z. Elektrochem.*, **59**, 545 (1955).

Non-Classified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Georgia Institute of Technology	Non-Classified
	2b. GROUP

3. REPORT TITLE

Complex Metal Hydrides.
High Energy Fuel Components for Solid Propellant Rocket Motors.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Annual Report (March 1, 1971-February 28, 1972)

5. AUTHOR(S) (First name, middle initial, last name)

Eugene C. Ashby

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 26, 1972	157	56

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
N00014-67-A-0159-005	
b. PROJECT NO.	
c. NA	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

During the fourth contract period, work has continued concerning the preparation and structure elucidation of complex metal hydrides of the main group elements. Six papers have appeared in Inorganic Chemistry since the last report period describing work carried out on this project. These papers are contained in the Appendix of this report. Major developments during the past report period include: (1) A direct synthesis of iminoalanes, $(RNAlH)_n$ compounds. These compounds should be excellent candidates as high energy binders. (2) New complex metal hydrides of magnesium, zinc and copper have been prepared. These compounds should be excellent candidates as high energy propellants and burning rate accelerators. (3) The development of a high vacuum DTA-TGA for the study of the decomposition of complex metal hydrides. (4) A solution to the problem of the existence of $HMgAlH_4$ and $HMgBH_4$ and to the identification of the products formed on reaction of $LiAlH_4$ and $NaAlH_4$ with organomagnesium compounds.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
	2b. GROUP

3. REPORT TITLE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.		
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	
d.		

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Complex Metal Hydrides						
High Energy Fuels						
Organometallic Compounds						
High Energy Binders						
Burning Rate Accelerators						

Non-Classified
Security Classification

G-33-605

Annual Report

to the

Office of Naval Research

"Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors."

E. C. Ashby, Principal Investigator

Georgia Institute of Technology, Atlanta, Georgia 30332

March 1, 1973 - December 31, 1973

This Research was Sponsored by the Office of Naval Research

under Contract No1 N00014-67-A-0519-C05AD and

ONR Contract Authority No. NR 093-050/7-11-69(473)

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Appendix

Attached Publications

In Press

Report Abstract

Several projects were pursued during the past nine months of this report period. The following projects were completed.

(1) Diethyl Ether Soluble Aluminum Hydride. The preparation of AlH_3 has been reported previously; however, it was reported to precipitate from diethyl ether solvent within minutes after preparation. We have found several methods for the preparation of aluminum hydride which is soluble in diethyl ether.

(2) Preparation of the First Stable Complex Metal Hydride of Copper, $LiCuH_2$. We have prepared $LiCuH_2$ by the reaction of $LiCu(CH_3)_2$ with $LiAlH_4$ in diethyl ether solvent. The compound is stable at room temperature under an N_2 atmosphere. Attempts were made to prepare Li_3CuH_4, Li_2CuH_3 and LiCuOR(H) compounds with no success. All of these compounds are not as stable as $LiCuH_2$ and decompose at room temperature.

(3) Redistribution of Aluminum Hydride with Groups I and II A and B Metal Halides. The redistribution of aluminum hydride with various Groups I and II A and B metal halides has been studied in detail. The hydrogen-halogen exchange in the system AlH_3-MX_2 (where M = Ca, Mg, Zn, Cd and Cu and X = Cl, Br and I) depends on the electronegativities of the metals. Calcium bromide and $MgBr_2$ do not react whereas $ZnCl_2$ and $ZnBr_2$ react to produce a new complex metal hydride H_3Zn_2X (where X = Cl and Br). The reaction of ZnI_2 with aluminum hydride in ether formed $ZnI_2 \cdot AlH_3$. Cadmium bromide reacted very slowly at -40° to produce HCdX.

(4) Attempted Desolvation of Ether Soluble Aluminum Hydride. Several attempts were made to desolvate the aluminum hydride prepared in ether solution. DTA-TGA indicated that the ether could be removed at 70°C; however, it was found that the temperature required (70°C) to remove

all of the ether also caused decomposition of the product.

(5) Reactions of $MZn_x(CH_3)_{2x}H$ Compounds with Aluminum Hydride. When AlH_3 was allowed to react with $LiZn(CH_3)_2H$, $LiZn(CH_3)_4H$ and $NaZn_2(CH_3)_4H$ in THF in 1:1 molar ratio, $LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4AlH_4$ and $NaZn_2(CH_3)_4AlH_4$ were formed. $LiZn_2(CH_3)_4AlH_4$ and $LiZn(CH_3)_2AlH_4$ were also formed in the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in THF in 1:2 and 1:1 molar ratio. Likewise, $NaZn_2(CH_3)_4AlH_4$ and $NaZn(CH_3)_2AlH_4$ were formed in the reaction of $NaAlH_4$ with $(CH_3)_2Zn$ in THF in 1:2 and 1:1 molar ratio. The mechanisms of formation of KZn_2H_5 or $NaZn_2H_5$ from the reaction of AlH_3 with $KZn(CH_3)_2H$ as $NaZnMe_2H$ were studied in detail. The mechanism of formation of KZn_2H_5 by the reaction of $KZn_2(CH_3)_4H$ with AlH_3 and the formation of ZnH_2 by the reaction of $(CH_3)_2Zn$ with $MAlH_4$ compounds was also studied.

Papers Published Since the Last Report

(1) E. C. Ashby, J. R. Sanders, P. Claudy and R. D. Schwartz, "A Study of the Reactions of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in Diethyl Ether and Tetrahydrofuran," Inorg. Chem., 12, 2860 (1973).

(2) E. C. Ashby and J.Watkins, "A New and Convenient Method for the Preparation of Complex Metal Hydrides of Group II Metals. Synthesis of Complex Metal Hydrides of Zinc," Inorg. Chem., 12, 2493 (1973).

(3) E. C. Ashby, J. R. Sanders, P. Claudy and R. Schwartz, "Diethyl Ether Soluble Aluminum Hydride," J. Amer. Chem. Soc., 95, 6485 (1973).

Papers in Press

(1) E. C. Ashby, P. Claudy and R. D. Schwartz, "Concerning the Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether," Inorg. Chem., (accepted for publication).

(2) E. C. Ashby, T. F. Korenowski and R. Schwartz, "Preparation of the First Stable Complex Metal Hydride of Copper, $LiCuH_2$", Inorg. Chem., (accepted for publication).

Diethyl Ether Soluble Aluminum Hydride[1]

(1) We are indebted to the Office of Naval Research (Contract No. N00014-67A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

We would like to report the preparation of diethyl ether soluble aluminum hydride prepared by three different reactions: (1) the reaction of lithium aluminum hydride and beryllium chloride, (2) the reaction of 100% H_2SO_4 with lithium aluminum hydride, and (3) the reaction of lithium aluminum hydride and zinc chloride. The yield in all three cases is quantitative.

$$2\ LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2\ AlH_3 \qquad (1)$$

$$2\ LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2\ AlH_3 \qquad (2)$$

$$2\ LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2\ LiCl\downarrow + ZnH_2\downarrow + 2\ AlH_3 \qquad (3)$$

Previous to this report soluble aluminum hydride could only be prepared in tetrahydrofuran. All attempts to prepare aluminum hydride in diethyl ether according to the method of Schlesinger (eq. 4) resulted

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} LiCl\downarrow + 4\ AlH_3\downarrow \qquad (4)$$

in significant precipitation of the aluminum hydride within 20 min after the rapid addition of reactants.[2,3]

(2) E. A. Finholt, A. C. Bond, and H. I. Schlesinger, J. Amer. Chem. Soc., 69, 1199 (1947).

(3) R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, Inorg. Chem., 2, 650 (1963).

To 20 mmole of $LiAlH_4$ in 150 ml of ether was added 10 mmole of $BeCl_2$. The solution was stirred for 2 hr and filtered. Analysis of the filtrate gave an Al:H:Li ratio of 1.0:2.97:0.002. No beryllium or chlorine was detected in the solution. Reversing the order of addition of the reactants yielded the same results. No precipitate of AlH_3 from solution was observed after 24 hr. The concentration of the solution dropped 4% in 1 week and 20% in 2 weeks. The infrared spectrum of the resulting solution[3] of AlH_3 (before precipitation) prepared by the Schlesinger method showed an Al-H stretching vibration at 1801 cm^{-1}. The AlH_3 which we have prepared has absorption bands at 1788 cm^{-1} owing to the Al-H stretching vibration and at 765 cm^{-1} owing to the Al-H deformation vibration.

Removal of the solvent under vacuum yields a white solid which was shown by elemental analysis to have the empirical formula of $AlH_3 \cdot 0.24(C_2H_5)_2O$. The X-ray powder diffraction pattern of this solid shows five main lines: 11.5 Å (s); 4.55 Å (m); 3.85 Å (m); 2.85 Å (m); and 2.32 Å (m). Bousquet, Choury, and Claudy,[4] have reported a powder

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(4) J. Bousquet, J. J. Choury, and P. Claudy, Bull. Soc. Chim. Fr., 3848 (1967).

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pattern for $AlH_3 \cdot 0.25(C_2H_5)_2O$. Their lines match ours with the exception of the line at 3.85 Å.

DTA-TGA analysis of the solid AlH_3 etherate prepared from $LiAlH_4$ and $BeCl_2$ shows that evolution of ether begins at 50°. Evolution of hydrogen begins at 90° and is centered at 110°. Molecular association studies on a freshly prepared sample of AlH_3 in ether indicate that AlH_3

prepared from $LiAlH_4$ and $BeCl_2$ is monomeric at a concentration of 0.13 - 0.16 M.

The reduction of ketones was investigated in order to evaluate ether soluble AlH_3 as a stereoselective reducing agent. With 4-tert-butylcyclohexanone, AlH_3 in diethyl ether gave 46% axial alcohol, compared with 13% axial alcohol using AlH_3 in THF and 12% axial alcohol using $LiAlH_4$ in ether.

The preparation of soluble AlH_3 in diethyl ether provides an opportunity to prepare compounds that normally disproportionate in THF solvent. For example, we have prepared HBeCl by reaction of AlH_3 with $BeCl_2$ (eq. 5). HBeCl was prepared unequivocally from BeH_2 and $BeCl_2$

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \qquad (5)$$

in diethyl ether establishing the infrared bands for HBeCl at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl had disappeared in DBeCl. Molecular weight determination of HBeCl in ether shows the compounds to be dimeric indicating that the BeH frequency at 1330 cm^{-1} is a bridge stretching mode.[5]

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(5) N. A. Bell and G. E. Coates, J. Chem. Soc., 892 (1965).

Exactly why stable ether solutions of AlH_3 are so easily prepared by the presently reported methods (eq. 1-3), whereas all reports in the past claimed AlH_3 precipitates from ether, is not understood. We are, however, investigating this aspect further.[6]

(6) Note Added in Proof. We have just found the preparation of AlH_3 by the Schlesinger method also results in ether-soluble AlH_3 under comparable reaction conditions. We are presently investigating the effect of $LiAlH_4$ purity and lithium content in the product AlH_3 as sources of this unique behavior.

Since MH_2 compounds of group II metals are insoluble in all organic solvents, it has been impossible to assign exact vibrational frequencies for the M-H band. It appears now that stable HMX compounds can be prepared from MX_2 and AlH_3 in ether, thus providing a means of obtaining stretching and deformation frequencies for M-H compounds. In this connection we are continuing our studies concerning reactions of AlH_3 in ether with groups I, II, and III metal halides.

Preparation of the First Stable Complex Metal Hydride of Copper, $LiCuH_2$

Summary

Reaction of $LiCu(CH_3)_2$ at low temperature with $LiAlH_4$ in diethyl ether results in the formation of a highly pyrophoric but stable solid whose analysis is consistent with the formula $LiCuH_2$, stable as an etherate.

Recently, considerable interest has been generated in copper chemistry, specifically in the area of synthetic applications involving lithium alkylcuprates[1] and copper hydride.[2,3] In view of the unusual

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(1) J. F. Normant, Synthesis, 63-80 (1972). G. H. Posner, Organic Reactions, 19, 1-113 (1972).

(2) J. A. Dilts and D. F. Shriver, J. Amer. Chem. Soc., 90, 5796 (1968).

(3) S. A. Bezman, M. R. Churchill, J. A. Osborn and J. Wormald, J. Amer. Chem. Soc., 93, 2063 (1971); Inorg. Chem., 11, 1888 (1972).

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chemistry of both of these reagents, we have been interested in the preparation of stable complex metal hydrides of copper in order to study there usefulness as reducing agents in organic chemistry.

Copper hydride prepared in ether is not stable at room temperature, decomposing with evolution of hydrogen to form a black solid.[4] Stable

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(4) J. C. Warf and W. Feitkneckt, Helv. Chim. Acta., 33, 613 (1950).

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solutions of CuH in pyridine have been prepared by Dilts and Shriver[2] who have shown that the solubility of CuH is due to its complexation with

the Lewis base. Stable complexes of CuH with triphenylphosphine have also been prepared by Churchill and co-workers.[3] The X-ray crystal structure determination showed the compound to be hexameric. This ability of CuH to undergo complex formation suggested to us that it should be possible to synthesize complex metal hydrides of copper. Monnier has claimed the preparation of $CuAlH_4$ at -80° by the reaction of Li_2CuBr_4 with $LiAlH_4$. However, the $CuAlH_4$ formed was not stable above -80° and decomposed to Cu, CuH, Al and H_2.[5] Our experience with complex metal

(5) G. Monnier, Ann. Chem., 2, 14 (1957).

hydrides of zinc (e.g., $LiZnH_3$, Li_2ZnH_4, etc.) suggests that complex metal hydrides of copper should be more stable than CuH itself.[6]

(6) J. J. Watkins and E. C. Ashby, J.C.S. Chem. Comm., 1972, 998.

With this objective in mind we prepared a complex metal hydride of copper, which is more stable than CuH, by the reaction of lithium dimethylcuprate with lithium aluminum hydride in diethyl ether. To a slurry of 18 mmole CuI in 200 ml diethyl ether at -78° was added 36 mmole methyl lithium in ether. The solution was stirred for 1 hr at -78° at which

$$CH_3Li + CuI \rightarrow CH_3CuI \quad (1)$$

$$CH_3Cu + CH_3Li \rightarrow LiCu(CH_3)_2 \quad (2)$$

$$LiCu(CH_3)_2 + LiAlH_4 \rightarrow LiCuH_2 + LiAl(CH_3)_2H_2 \quad (3)$$

time all the CuI had dissolved. To this was added 18 mmole of $LiAlH_4$ in ether. No precipitate formed at -78°; however, while warming the

solution to room temperature, a yellow solid precipitated from solution. The reaction mixture was filtered and the yellow solid isolated as an ether slurry. This slurry gave the following analysis: Li:Cu:H:Al; 1.03:1.0:2.06:0.08. The infrared spectrum of the filtrate corresponded to that of an authentic sample of $LiAlH_2(CH_3)_2$ prepared by the redistribution of $LiAl(CH_3)_4$ and $LiAlH_4$. The yellow solid was isolated by filtration and dried under vacuum.[7] DTA-TGA analysis of solid $LiCuH_2$ etherate

(7) Prolonged subjection of the yellow solid ($LiCuH_2$) to vacuum in order to remove the ether of solvation resulted in decomposition of the sample. The dry yellow solid was stable at room temperature for at least several days; however, due to its great sensitivity to O_2 and H_2O, it was generally stored as an ether slurry prior to use.

shows violent decomposition at 70° with the evolution of ether. No sharp lines, but rather two broad diffuse lines were observed in the X-ray powder pattern of the solid $LiCuH_2$. When stored as an ether slurry, $LiCuH_2$ is stable at room temperature for several days, unlike CuH alone (prepared in diethyl ether) which decomposes immediately upon warming to room temperature.[4]

We have also attempted the preparation of another stoichiometric complex metal hydride of copper, Li_3CuH_4. The method of preparation was similar to that for $LiCuH_2$. Four moles of MeLi were added to 1 mole of CuI at -78° in ether to give Li_3CuMe_4. This was then reduced with $LiAlH_4$. The yellow solid obtained upon warming to room temperature gave the following analysis: Li:Al:Cu:H. 3.58:0.36:1.0:5.6. Even after extensive washing with ether the solid still gave the same Al:Cu ratio. We suspect that the aluminum contaminent is Li_3AlH_6. House, Respess and Whitesides[8] have

(8) H. O. House, W. L. Respess and G. M. Whitesides, J. Org. Chem., 31, 3128 (1966).

studied the nmr of "Li_3CuMe_4" at various temperatures and have found that at low temperatures the signals can be resolved to indicate an equilibrium as shown in equation 4. The nmr indicate that this equilibrium lies

$$Li_3CuMe_4 \rightleftharpoons 2\ LiMe + LiCuMe_2 \qquad (4)$$

substantially to the right. The addition of $LiAlH_4$ to this mixture would be expected to generate LiH by reduction of the LiMe with $LiAlH_4$. The LiH formed *in situ* could then react with $LiAlH_4$ to yield Li_3AlH_6. It was hoped that if LiH formed, it would react more rapidly with $LiCuH_2$ to form Li_2CuH_3 and Li_3CuH_4 than with $LiAlH_4$ to form Li_3AlH_6, but apparently this is not the case.

Lithium copper hydride, $LiCuH_2$ was prepared in THF by the reduction of $LiCuMe_2$ with $LiAlH_4$ in that solvent at -78°. However, the $LiCuH_2$ did not precipitate from THF upon warming to room temperature. Upon addition of ether to the THF solution, a yellow-brown solid precipitated which gave the following analysis: Li:Cu:H:Al; 1.09:1.0:1.81:0.18. In subsequent preparations the solid was washed with small amounts of THF and these gave the following analysis: Al:Cu:H; 0.07:1.0:1.95. The solid $LiCuH_2$ prepared in THF was stable at room temperature for several days. However, THF solutions containing $LiCuH_2$ began to turn dark green after several hours. $LiCuH_2$ prepared in ether was found to be slightly soluble in pyridine (0.02 M) and insoluble in DME.

Since the samples of $LiCuH_2$ prepared from $LiCuMe_2$ and $LiAlH_4$ have several mole per cent aluminum, we decided to examine other reducing agents which do not contain aluminum in order to eliminate the impurity. Lithium

borohydride was found not to react with $LiCuMe_2$ to yield $LiCuH_2$. Bu_3SnH did react with $LiCuMe_2$ in ether at -78° to give a deep red solution, however, upon warming to room temperature the sample decomposed to a black solid with evolution of gas. We also attempted to reduce $(Bu_2S)_2CuI$ with two moles of LiH (eq. 5) , to yield $LiCuH_2$. However, the tan solid

$$2\ LiH + (Bu_2S)_2CuI \xrightarrow[-78°]{\text{ether}} \begin{cases} LiCuH_2 + 2\ Bu_2S \\ CuH + LiH + 2\ Bu_2S \end{cases} \qquad (5)$$

which formed decomposed upon warming to room temperature to Cu metal with evolution of a gas. We concluded that LiH did reduce the CuI to CuH but that the CuH did not add the second mole of LiH to give $LiCuH_2$.

Posner, Whitten and Sterling[9] have prepared compounds of empirical

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(9) G. H. Posner, C. E. Whitter and J. J. Sterling, J. Am. Chem. Soc., 95, 7788 (1973).

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formula: LiCuHet(R) where Het = OTBu; OC_6H_5; SC_6H_5. Since $LiCuH_2$ is much more stable than $LiCuMe_2$, we hoped to prepare stable compounds of the formula LiCuHet(H) by reducing the LiCuHet(R) with $LiAlH_4$. The general method of preparation which we attempted involved preparation of CuHet compounds from LiHet and CuI in THF (eq. 6). The resulting solution

$$LiHet + CuI \rightarrow CuHet + LiI \qquad (6)$$

was then cooled to -78° and LiC_4H_9 was added. This was followed by the addition of a stoichiometric amount of $LiAlH_4$ according to equation 7.

$$4\ LiCuHet(R) + LiAlH_4 \rightarrow 4\ LiCuHet(H) + LiAlR_4 \qquad (7)$$

However, in the case of Het = O-tC_4H_9 and OC_6H_5 a black solid precipitated

from solution at -78°. In the case of Het = SC_6H_5, the black solid precipitated from solution with evolution of a gas upon warming to room temperature.

We have found in our work with complex metal hydrides of zinc and magnesium that by changing the cation of an "ate" complex from Li to K the compound becomes more stable. We therefore attempted to prepare KCu(OtBu)H hoping that it would be more stable than the corresponding lithium compound. We therefore allowed KH and CuOt Bu to react in ether at -78° in a 1:1 ratio in order to obtain KCuOtBu(H). However, upon warming to room temperature the solution turned black with evolution of a gas. This reaction is probably similar to the case of LiH and $(Bu_2S)_2CuI$ in that the KH simply reduces CuOtBu to CuH rather than complexing the CuOtBu to form KCuOtBu(H).

$$2\ KH + CuOtBu \begin{cases} \not\longrightarrow\ KCu(OtBu)H \\ \longrightarrow\ KOtBu + CuH + KH \end{cases} \qquad (8)$$

We also attempted to prepare $KCuH_2$ hoping that the change in cation from Li to K would produce a more stable compound. The method of preparation used is outlined in equations 9 and 10. However, upon addition

$$2\ KOtBu + CuI \xrightarrow{THF} KCu(OtBu)_2 + KI \qquad (9)$$

$$KCu(OtBu)_2 + LiAlH_4 \xrightarrow[-78°]{THF} KCuH_2 + LiAlH_2(OtBu)_2 \qquad (10)$$

of the $LiAlH_4$ a deep red solution was formed which upon warming to room temperature precipitated copper metal with evolution of a gas.

We have also studied the reducing properties of $LiCuH_2$ in ether and THF by allowing it to react with various ketones. $LiCuH_2$ was allowed to react with 3,3,5-trimethylcyclohexanone in ether at 0° for 2 hr.

Quenching the reaction mixture with 10% HCl and analyzing the product according to glc analysis showed the product ratio to be 70:30 axial alcohol: equatorial alcohol. Reduction of isophorone under the same conditions yielded 3,3,5-trimethylcyclohex-2-ene-1-ol with no dihydroisophorone. $LiCuH_2$ was allowed to react with 4-tert-butylcyclohexanone in THF at room temperature. The following product ratios were obtained; 79:21 axial: equatorial alcohol. Attempted reduction of isophorone gave no volitile products. When the reduction was run at 0° the ratio products from 4-t butylcyclohexanone had changed to 58:42 axial:equatorial alcohol. Again, no volitile products were found from the reaction of isophorone with $LiCuH_2$.

In conclusion we have prepared the first complex metal hydride of copper, $LiCuH_2$, in both ether and THF. $LiCuH_2$ was found to be stable at room temperature for several days. However, repeated attempts to prepare compounds such as LiCuHet(H) or $KCuH_2$ resulted in decomposition of the product mixtures to copper and hydrogen.

Redistribution of Aluminum Hydride with Groups I and II A and B Metal Halides

Abstract

The redistribution reaction of aluminum hydride with various group II A and B metal halides in diethyl ether has been studied in detail. The hydrogen-halogen exchange in the system AlH_3-MX_2 (where M = Ca, Mg, Zn, Cd and Cu; X = Cl, Br, and I) depends on the electronegativities of the metals concerned. Thus, calcium bromide and magnesium bromide do not undergo exchange with aluminum hydride whereas zinc chloride and zinc bromide react with aluminum hydride to produce a new complex metal hydride of the type H_3Zn_2X (X = Cl, or Br). The reaction of zinc iodide with aluminum hydride yielded a complex of the composition $ZnI_2 \cdot AlH_3$. Cadmium bromide reacted very slowly with aluminum hydride at -40° to yield a compound of the formula HCdX. The compounds were characterized by X-ray powder patterns, infrared spectroscopy and elemental analyses.

Introduction

In view of our recent study of the redistribution reaction of aluminum hydride with beryllium chloride in diethyl ether and the possibility of the existence of HMX compounds (where M = Groups I and II A and B metals and X = Cl, Br, or I), we have extended our investigation of redistribution reactions involving AlH_3 to include other group II A and B metal halides in addition to $BeCl_2$ and $BeBr_2$.[1]

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \qquad (1)$$

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(1) E. C. Ashby, P. Claudy and R. D. Schwartz, Inorg. Chem., (in press).

Although there have been several reports of the preparation and characterization of Groups I and II A and B metal hydrides in the literature[2], very little is know about the corresponding hydridometal

(2) E. Wiberg and E. Amberger, Hydrides of the Elements of Main Groups I-IV, Elsvier Publishing Company, 1971, pp. 48-80, 422 and references therein.

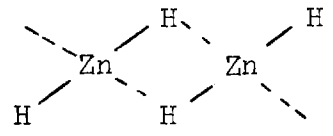
halides (HMX). In 1951 Wiberg and Henle[3] reported that the addition of an

(3) E. Wiberg and Walter Henle, Z. Naturforsch, 6b, 393 (1951).

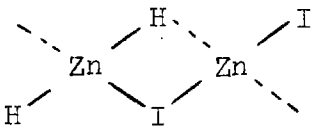
etherial solution of zinc chloride to a solution of aluminum hydride and aluminum chloride (1:1 mole ratio) in ether produced impure zinc hydride. These workers also reported[4] the preparation of a white solid corresponding

(4) E. Wiberg and Walter Henle, Z. Naturforsch, 7b, 249 (1952).

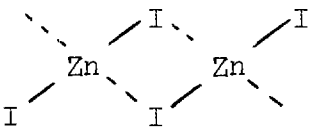
to the formula HZnI by the reaction of zinc iodide with lithium hydride in diethyl ether. As the above compound could not be isolated in pure form and contained different amounts of iodine, depending on the conditions of isolation, alternating structures (a,b,c,) were suggested for HZnI.



(a)



(b)



(c)

Wiberg and Henle[5] also studied the reaction between cadmium iodide in

(5) E. Wiberg and W. Henle, Z. Naturforsch, 6b, 461 (1951).

THF and lithium aluminum hydride in diethyl ether at -76° to -40°. In this case only cadmium hydride was obtained as a white solid which decomposed spontaneously at a slow rate at -20° to the elements at room temperature. No evidence was obtained for either $Cd(AlH_4)_2$ or HCdI. The preparation of hydridomagnesium halides has been reported by several workers;[6-8] however, it has been found recently[9] that these compounds

(6) E. Wiberg and P. Strebel, Ann., 607, 9 (1957).

(7) T. N. Dymova and N. G. Eliseeva, Russ. J. Inorg. Chem., 8, 820 (1963).

(8) M. J. Rice, Jr., and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ORN-494 (04), 1956.

(9) E. C. Ashby, R. A. Kovar and K. Kawakami, Inorg. Chem., 9, 317 (1970).

actually exist as physical mixtures of magnesium hydride and the corresponding magnesium halide.

Continuing our studies on the redistribution reactions of aluminum hydride with Groups I and II A and B metal halides, we have isolated new complexes of zinc halides of the type H_3Zn_2X (X = Cl, or Br) and $ZnI_2 \cdot AlH_3$. No conclusive evidence has been found for the existence of "HMX" species. In this paper we report the reactions of aluminum hydride in ether solvent with calcium bromide, magnesium bromide, zinc halides and cadmium bromide in several stoichiometric ratios.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture[10]

(10) E. C. Ashby and R. D. Schwartz, J. Chem. Ed., 51, 65 (1974).

or on the bench using typical Schlenk-tube techniques.[11]

(11) D. H. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, 1969.

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 621 Grating Infrared Spectrophotometer using NaCl and CsI liquid cells. Solid samples were prepared as mulls in nujol and the spectra were measured using polyethylene and CsI plates. X-ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46 cm diameter camera with Ni-filtered Kα radiations. The samples were exposed for 6.0 hr. d-Spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. TGA analyses were carried out using a Mettler Thermoanalyzer with high vacuum attachment.[12]

(12) E. C. Ashby and Pierre Claudy, J. Chem. Ed., (in press).

Reagents. Diethyl ether (Fisher anhydrous ether) was distilled over lithium aluminum hydride immediately prior to use. All metal halides were Fisher Certified reagent grade. Aluminum halides were purified by vacuum sublimation and ether solutions were prepared at -20° by slow

addition of the aluminum halide to pre-cooled ether. Magnesium bromide ether solution was obtained by the method described previously.[13]

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(13) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

Zinc halides were dried by heating the compounds slowly with a Bunsen flame under vacuum until they sublimed completely. Zinc halide ether solutions were obtained by dissolving the sublimed material in ether at room temperature. Anhydrous cadmium bromide was dried further by heating at 115° overnight under vacuum. Ether soluble aluminum hydride was prepared by the reaction of beryllium chloride and lithium aluminum hydride in diethyl ether.[14]

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(14) E. C. Ashby, J. R. Sanders, P. Claudy and R. D. Schwartz, J. Amer. Chem. Soc., 95, 6485 (1973).

Analytical Procedures. Hydrogen analysis was carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexiметric titration with EDTA. Zinc, magnesium and cadmium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Analysis for chloride, bromide or iodide was carried out using a modified Volhard procedure.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ and $AlBr_3$ in Diethyl Ether. The hydridoaluminum halides H_yAlX_{3-y} (where X = Cl, or Br) were prepared by mixing solutions of AlH_3 and aluminum halides in ether at 0° in the appropriate ratios. Redistribution reactions between AlH_3

and aluminum halides have been discussed by a number of authors.[15] The

(15) E. Wiberg and M. Schmidt, Z. Naturforsch, 6b, 460 (1951); S. M. Arkhipov and V. I. Mikheeva, Zh. Neorg. Khim., 11, 2006 (1966); E. C. Ashby and J. Prather, J. Am. Chem. Soc., 88, 729 (1966).

infrared spectra are reported in Figure 1.

Reaction of $MgBr_2$ with AlH_3. (1) In 1:1 mole ratio. A solution of aluminum hydride (10 ml, 2.732 mmoles) in ether was added slowly with stirring to a solution of magnesium bromide (21.45 ml, 2.732 mmoles) in ether. There was no immediate precipitate and the mixture remained clear even after 24 hours stirring. The infrared spectrum of the clear solution showed strong bands at 1785 cm^{-1} and 760 cm^{-1} and a band of medium intensity at 380 cm^{-1}. The infrared spectrum of the solid obtained by complete removal of ether from the reaction mixture showed bands at 1800 (w) and 1600 cm^{-1} (br,s). The elemental analysis of the solid gave the ratio Mg:Al:H:Br = 1.0:1.04:2.90:2.11. X-ray powder diffraction patterns of the solid showed it to be essentially a physical mixture of $MgBr_2$ and AlH_3. When the reaction mixture was allowed to stand for a few weeks, some grey solid compound separated out. The solid was filtered, dried under vacuum and analyzed: Mg:Al:H:Br = 1.24:1.0:1.02:1.95. The infrared spectrum showed a very weak broad band at ~ 1600 cm^{-1}.

(2) In 1:2 mole ratio. Ether solutions of aluminum hydride (8.578 mmoles) and magnesium bromide (4.289 mmoles) were mixed together as described before. In this case also there was no immediate precipitate and the mixture stayed clear for more than 24 hr. The infrared spectra of the clear mixture and the solid obtained after complete removal of ether, were identical with the spectra obtained in (1). Similarly

X-ray powder patterns from (1) and (2) were the same. However, it was noticed that the formation of grey solid compound was faster in this case and in one week 33% of the solid (calculated on the basis of solid $MgBr_2 \cdot AlH_3$) precipitated from solution. Analysis of grey powder showed: Mg:Al:H:Br = 1.0:1.70:2.22:1.41.

Reaction of $ZnCl_2$ with AlH_3. Preparation of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$. In a typical reaction, a solution of aluminum hydride in ether was added slowly to a solution of zinc chloride in ether in an appropriate ratio (see below). An immediate precipitation of a white solid took place. The mixture was stirred for ten minutes and then filtered. The white residue was washed with ether, dried under vacuum and stored at -20°. Anal. Calcd. for $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$: H (hydrolysable), 1.57; Zn, 66.99; Cl, 18.16. Found: H (hydrolysable), 1.59; Zn, 66.52; Cl, 17.82. The yield of product based on this analysis is 95%. The infrared spectrum of the white solid showed a very broad band with a maxima at ~ 1550 cm^{-1} and a weak band at ~ 460 cm^{-1}. The X-ray poweder diffraction data given in Table 1 showed lines different from $ZnCl_2$ and AlH_3.

The reaction was repeated in the following ratios of AlH_3:$ZnCl_2$: 1:1, 1:2, 1:3 and 4:1. The white precipitate obtained in each case was subjected to complete elemental analysis and characterized by infrared spectra and X-ray powder diffraction patterns. Similarly, the filtrate after isolation of white solid, was characterized by infrared spectroscopy and elemental analysis. The results are described separately.

(a) AlH_3:$ZnCl_2$, 1:1 mole ratio. Aluminum hydride, 6.75 mmoles in ether solvent was mixed with zinc chloride, 6.75 mmoles in ether solvent. Analysis of the resulting white solid gave Zn:H:Cl:Al = 1.00:1.74:0.41:0.07. Infrared analysis of the solid (nujol mull) showed two broad bands

at ~ 1550 and 600-350 cm^{-1} centered at 460 cm^{-1}. The X-ray powder pattern of the solid was different from the patterns obtained for $ZnCl_2$ and AlH_3 (Table 1). Elemental analysis of the filtrate showed: H:Al:Cl:Zn = 1.60:1.00:1.57:0.00 and infrared analysis showed the following bands: 1898 (s), 1850 (ms), 775 (s) and 720 (s) cm^{-1}.

(b) AlH_3:$ZnCl_2$, 1:2 mole ratio. AlH_3, 6.846 mmoles in ether solvent, was mixed with $ZnCl_2$, 13.692 mmoles in ether solvent. Elemental analysis of the solid residue showed: Zn:H:Cl:Al = 1.00:1.56:486:0.05. The infrared spectrum and X-ray powder diffraction pattern were similar to the solid described earlier (a).. The infrared spectrum of the filtrate did not show any bands between 2000 - 1600 cm^{-1} and 800 - 700 cm^{-1}.

(c) AlH_3:$ZnCl_2$, 1:3 mole ratio. AlH_3, 2.259 mmoles in ether solvent was mixed with 6.779 mmoles of $ZnCl_2$ in ether solvent. Analysis of the resulting precipitate gave Zn:H:Cl:Al = 1.00:1.49:0.57:0.00. An infrared spectrum and X-ray powder pattern were obtained as in the previous cases. The analysis of the filtrate showed Al:Zn:Cl:H = 1.00: 0.64:3.98:0.00. Infrared analysis did not show any absorption bands due to a hydridoaluminum halide.

(d) AlH_3:$ZnCl_2$, 4:1 mole ratio. AlH_3, 5.957 mmoles in ether solvent. Analysis of the white solid gave Zn:H:Cl:Al = 1.0:1.91:0.43: 0.07. The infrared spectrum of the filtrate showed strong bands at 1900, 1850 (sh), 1785 and 760 cm^{-1}.

Reaction of $HAlCl_2$ and $ZnCl_2$. 40 ml (7.404 mmoles) of $HAlCl_2$ solution in ether was added slowly to a solution of zinc chloride (21.84 ml, 7.404 mmoles) in ether. There was an immediate precipitation of a white solid.. The mixture was stirred for about ten minutes and then filtered. The residue was washed, dried under vacuum and analysed:

Zn:H:Cl:Al = 1.00:1.40:0.76:0.12. The infrared spectrum of the filtrate showed a broad band near 1500 - 1400 cm^{-1}.

Reaction of $ZnBr_2$ and AlH_3. Preparation of $H_3Zn_2Br \cdot 0.29(C_2H_5)_2O$. A solution of aluminum hydride was added slowly with stirring to a solution of zinc bromide in ether and the mixture stirred about ten minutes. The white solid was filtered, washed with ether and dried under vacuum. The compound was stored at -20°. Anal. Calcd. for $H_3Zn_2Br \cdot 0.29(C_2H_5)_2O$: H (hydrolysable), 1.28; Zn, 55.51; Br, 33.93. Found: H (hydrolysable), 1.17; Zn, 61.42; Br, 26.58. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1}. X-ray powder diffraction data is given in Table 1. The above reaction was carried out in several mole ratios of AlH_3:$ZnBr_2$ and the results are described below.

(a) AlH_3:$ZnBr_2$, 1:1 mole ratio. AlH_3, 6.357 mmoles in ether solvent was added to $ZnBr_2$, 6.357 mmoles in ether solvent. A white solid precipitated and was analyzed: Zn:H:Br:Al = 1.00:1.91:0.37:0.03. Infrared analysis of the solid (nujol mull) showed a broad band near 1600 cm^{-1}. The infrared spectrum of the filtrate showed the following bands: 1900 (s), 1850 (sh), 765 (s) and 700 cm^{-1} (ms). The filtrate on standing overnight at room temperature deposited some grey powder which was mostly metallic zinc.

(b) AlH_3:$ZnBr_2$, 1:2 mole ratio. AlH_3, 5.495 mmoles in ether solvent was added to $ZnBr_2$, 10.990 mmoles in ether solvent. Elemental analysis of the resulting solid gave Zn:H:Br:Al = 1.0:1.66:0.356:0.04. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1} whereas the infrared spectrum of the filtrate did not show any band between 2000 - 1600 cm^{-1} and between 800 - 700 cm^{-1}.

(c) AlH_3:$ZnBr_2$, 1:3 mole ratio. AlH_3, 7.334 mmoles in ether solvent was mixed with $ZnBr_2$, 22.002 mmoles in ether solvent. Analysis of the

white solid precipitate gave the molar ratio: Zn:H:Br:Al = 1.00:2.06:0.411: 0.04. The infrared spectrum of the filtrate did not show any absorption band due to hydridoaluminum compounds.

Reaction of AlH_3 and ZnI_2. Preparation of $ZnI_2 \cdot AlH_3 \cdot 1.79(C_2H_5)_2O$. Solutions of aluminum hydride and zinc iodide in ether solvent were allowed to react. The white solid which precipitated immediately after mixing was filtered, washed with ether, dried under vacuum and stored at -20°. Anal. Calcd. for $ZnI_2 \cdot AlH_3$, $1.79(C_2H_5)_2O$. Zn, 13.55; I, 52.64; Al, 5.59; H (hydrolysable), 0.627. Found: Zn, 13.86; I, 53.07; Al, 5.99; H(hydrolysable), 0.693. The infrared spectrum of the white solid showed the following bands in addition to bands due to diethyl ether: 1630 (vs, br), 670 (s), 520 (m) and 325 cm^{-1} (w). The X-ray powder diffraction pattern of the solid is listed in Table 1. The reaction was carried out in several mole ratios of AlH_3:ZnI_2 and the results are described below.

(a) AlH_3ZnI_2, 1:2 mole ratio. AlH_3, 1.473 mmoles in ether solvent was mixed with ZnI_2, 2.947 mmoles in ether solvent. Analysis of the white solid precipitate gave a molar ratio of Zn:Al:H:I = 1.0:1.07:2.99:1.97. An infrared spectrum and X-ray powder diffraction pattern were identical with those described for the reaction carried out in 1:1 ratio. Analysis of the filtrate showed: Zn:Al:H:I = 1.0:0.09:0.04:2.12. An infrared spectrum of the filtrate did not show any absorption bands near 2000-1600 cm^{-1} and 800-700 cm^{-1}. In a separate experiment, ether solutions of AlH_3 and ZnI_2 were mixed together in 1:2 mole ratio and the mixture was stirred at 0° for two days. The white solid was then filtered, washed with ether and dried under vacuum. The elemental analysis and the infrared spectrum of the white solid were identical to that described above.

(b) AlH_3:ZnI_2, 4:1 mole ratio. AlH_3, 5.825 mmoles in ether solvent was mixed with ZnI_2, 1.453 mmoles in ether solvent. A white solid which precipitated immediately after mixing showed a molar ratio of Zn:Al:H:I = 1.00:1.04:3.26:1.91. The infrared spectrum and X-ray

powder diffraction data were identical to that described above. However, the infrared spectrum of the filtrate showed absorption bands at 1785 (s) and 760 cm^{-1} (s).

Reaction of AlH_3 and $CaBr_2$. A solution of aluminum hydride (20.11 ml, 4.7938 mmoles) in diethyl ether was added to a slurry of $CaBr_2$ (0.9583 g, 4.7938 mmoles) in 100 ml ether. The mixture was stirred for three days at room temperature. It was then filtered, washed with ether and the residue dried under vacuum. Elemental analysis of the residue gave: Ca:Br:H = 1.00:1.97:0.02. An infrared spectrum of the filtrate showed bands due to aluminum hydride only at 1785 (s) and 760 cm^{-1} (s).

Reaction of $CdBr_2$ and AlH_3. 1.9495 g (7.161 mmoles) of $CdBr_2$ was transferred to a 250 ml Schlenk tube followed by the addition of 50 ml of diethyl ether. The mixture was stirred at -40° to -30° for about fifteen minutes and then a solution of aluminum hydride (26.0 ml, 7.161 mmoles) in diethyl ether was added to the $CdBr_2$ slurry dropwise keeping the temperature of the reaction mixture always below -30°. The mixture was stirred for four days at -40 to -30° during which time infrared spectra of the clear solution were recorded in order to follow the progress of the reaction. When the reaction was complete, a small portion of the solution was analyzed: H:Al:Br:Cd = 2.12:1.00:0.79:0.00. The infrared spectrum of the filtrate showed bands at 1860 (s, br), 760 (s) and 700 cm^{-1} (s). The solid residue (slightly grey) was washed twice with cold (-70°) ether allowing the precipitate to settle to the bottom of the Schlenk tube while removing the clear liquid by syringe under nitrogen. The solid was analysed: H:Cd:Br = 1.00:1.00:1.143. Hydrogen analysis was carried out by attaching the Schlenk tube with the solid directly to the vacuum line and allowing the solid to decompose at room temperature.

The above reaction was studied in detail under the following

conditions.

(1) Reaction product allowed to warm to room temperature. $CdBr_2$ and AlH_3 were mixed in 1:1 mole ratio in diethyl ether in the same way as described above. The mixture was stirred for 6 hr at -76° and then allowed to warm slowly to room temperature. When the temperature of the reaction mixture reached -20°, it started turning dark and at room temperature became completely black giving off hydrogen gas. The black solid was separated by filtration, washed with ether and dried under vacuum. The infrared spectrum of the solid did not show any absorption bands due to metal hydrides. The infrared spectrum of the filtrate on concentration showed bands at 1906 (s), 762 (s) and 700 cm^{-1} (s). Analysis of the filtrate showed: H:Al:Br = 0.576:1.00:2.00 and it contained 73% of the total aluminum. Elemental analysis of the black residue gave: Al:Cd:Br:H = 0.08:1.00:1.73:0.00.

(2) Reaction of $CdBr_2$ and AlH_3 in THF. Since $CdBr_2$ is more soluble in THF than diethyl ether, a solution of AlH_3 (3.31 ml, 1.320 mmoles) in THF was added to a solution of $CdBr_2$ (200 ml, 1.320 mmoles) in THF at -76°. The mixture was stirred at -35° for 4 hr and then allowed to settle overnight inside a dewar flask. It was noticed that even after 16 hr the mixture remained turbid. The supernatent liquid was then removed carefully, with a syringe and the remaining solid washed with cold THF. The resulting solid was analyzed: H:Cd:Br:Al = 1.00:1.00: 2.09:0.93.

(3) Reaction of $CdBr_2$ and AlH_3 in 3:1 mole ratio in Ether. $CdBr_2$ and AlH_3 were mixed in 3:1 mole ratio in ether and the mixture stirred for 6 hr at -40 to -35°. The mixture was allowed to settle and the infrared spectrum of the clear solution showed the absence of any hydrido-aluminum compound. The reaction mixture was then cooled to -76° and

transferred inside the glove box as fast as possible flushing the outer-port with nitrogen for ten minutes. It was then filtered and washed with cold (-40°) ether. The white solid residue turned black within a few seconds. The infrared spectrum of the filtrate on concentration did not show any absorption bands due to aluminum-hydrogen compounds. Analysis of the filtrate showed: H:Al:Cd:Br = 0.00:1.00:0.00:0.76, corresponding to 36.2% of the total aluminum.

Reaction of $CdBr_2$ and H_2AlBr in Ether. 61 ml (7.585 mmoles) of H_2AlBr in ether was added to a slurry of $CdBr_2$ (2.0649 g, 7.585 mmoles) in ether stirred at -40°. The mixture was stirred for five days at -40 to -30° until the reaction was complete. The infrared spectrum of the clear solution showed a strong and broad band at 1900 - 1800 cm^{-1} with a maximum at 1850 cm^{-1}. The position of the band did not change on further stirring. Analysis of the solution showed: H:Al:Br:Cd = 1.906:1.00:1.15:0.04, whereas the analysis of the residue on decomposition at room temperature and subsequent hydrolysis gave: H:Cd:Br:Al = 0.188:1.00:1.94:0.09.

Reaction of CuCl and AlH_3 in Ether. 42.71 ml (12.896 mmoles) of aluminum hydride solution in ether was added to a slurry of CuCl (1.276 g, 12.896 mmoles) in ether. The mixture was stirred for 6 hr at -76° and then allowed to warm to room temperature. At -40°, the color of the reaction mixture started to turn black and by the time the temperature rose to 0°, it was almost completely black giving off some gas. It was then filtered, washed with ether and the residue dried at room temperature. The infrared spectrum of the filtrate showed a strong band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1}, and a strong band at 775 cm^{-1}. Analysis of the filtrate gave a molar ratio of H:Al:Cl, 1.00:1.04:1.804 corresponding to 44.2% of total aluminum.

Results and Discussion

The reaction of aluminum hydride with Groups I and II A and B metal halides can be considered as a metathetical exchange reaction in which one or more hydrogen atoms of alane are exchanged with the halogen atom of the metal halide. The electronegativity differences for metal halides are calculated from the expression where Q = standard heat of

$$Q = 23 \Sigma (X_A - X_B)^2 \qquad (2)$$

formation and $X_A - X_B$ = electronegativity difference for the elements A and B. The electronegativity differences for metal halides are listed in Table II. A comparison of these electronegative difference values with the experimental observations show that if the electronegativity of the Group I or II metal halide is much higher than the corresponding aluminum halide, the exchange reaction does not take place. However, in the case of comparable or lower electronegativity differences the exchange does take place. This simply means that in the exchange reaction between AlH_3 and a metal halide the reaction will proceed to form the most thermodynamically products which are then resulting from the most electronegative group (halogen) residing in the most electropositive metal, thus carrying the greatest difference in electronegativity between the metal and halogen (Table II). Therefore, AlH_3 would not be expected to react with LiCl to form $AlCl_3$ and LiH, but would be expected to react with $ZnBr_2$ to form $AlBr_3$ and ZnH_2.

As reported previously,[14] the redistribution reactions were studied by mixing ether solutions of AlH_3 with MX_2 compounds in various mole ratios and carrying out complete elemental analysis on the resulting solution and on any precipitate that formed. The precipitate was also

studied by X-ray powder diffraction, DTA-TGA and infrared analysis. The solutions were also studied further by infrared spectroscopy. Since hydrogen exchange in the AlH_3-MX_2 system would be expected to form hydridoaluminum halides, it was necessary first to prepare these compounds in order to obtain the necessary infrared spectroscopic information for identification purposes. Ether soluble AlH_3 was found to exhibit bands in its infrared spectrum at 1785 and 770 cm^{-1}. These bands are assigned to the Al-H stretching and Al-H deformation vibrations, respectively. Although the infrared spectra of hydridoaluminum halides in diethyl ether have already been reported previously,[14] the compounds were prepared again by mixing AlH_3 and $AlCl_3$ in the proper ratio and the ir spectra were recorded.

$$2\ AlH_3 + AlX_3 \rightarrow 3\ AlH_2X \qquad (3)$$

$$AlH_3 + 2\ AlX_3 \rightarrow 3\ AlHX_2 \qquad (4)$$

(X = Br, Cl)

The hydridobromoalanes were prepared in the same way as the chloro compounds and the infrared spectra are shown in Figure 1. The infrared spectrum of H_2AlBr shows bands at 1850 (s), 770 (s), 720 (s), 480 (m), 447 (m) and 362 cm^{-1} (w) and the infrared spectrum of $HAlBr_2$ shows bands at 1900 (s), 770 (m), 447 (m), 410 (vw) and 360 cm^{-1} (w).

Calcium bromide does not under go an exchange reaction with alane as predicted due to the fact that calcium is more electropositive than aluminum. Elemental analysis as well as the infrared analysis of the products obtained after mixing an ether solution of AlH_3 with $CaBr_2$ result in a quantitative recovery of unreacted calcium bromide and alane. Similarly, magnesium bromide also does not react with alane in diethyl ether. Although there is no immediate precipitate after mixing an ether

solution of $MgBr_2$ with AlH_3, the possibility of some soluble metal complex hydride could not be ruled out completely. Therefore, in order to characterize the complex, if any, the infrared spectrum of magnesium bromide and alanes were run near far infrared region to establish metal-hydrogen (deformation) and metal-halogen stretching frequencies. The infrared spectra of both $MgBr_2$ and the reaction mixture showed only one medium intense band at 380 cm^{-1} other than weak bands for diethyl ether (Figure 3). This band may be assigned to the Mg-Br stretching vibration. For a comparison of the X-ray powder diffraction pattern of the solid obtained after complete ether removal with the pattern of the reaction mixture, powder diffraction patterns were obtained for $MgBr_2$ and AlH_3 containing almost the same number of solvent molecules (Table 1). The X-ray powder pattern of the product was consistent with a physical mixture of $MgBr_2$ and AlH_3. Similarly, the TGA analysis of the solid showed it to be either a very weak complex of AlH_3 or a free AlH_3 diethyl etherate mixed with $MgBr_2$. On standing for several days at room temperature the reaction mixture decomposed to hydrogen and aluminum which precipitated as a grey powder. The absence of infrared absorption bands characteristic of the Mg-H stretching vibration ruled out the possibility of the existence of either MgH_2 or HMgBr in the grey solid.

$\underline{ZnCl_2 \text{ and } AlH_3}$. In 1:1 mole ratio, zinc chloride and AlH_3 react to produce a stable white solid of empirical formula $H_3Zn_2Cl \cdot .35(C_2H_5)_2O$. The infrared spectrum of the filtrate showed absorption bands at 1900 (s), 1850 (s), 780 (s) and 720 cm^{-1} (s), indicating the presence of $HAlCl_2$ and H_2AlCl in solution. The results suggest that the reaction takes place in the following manner:

$$2\ ZnCl_2 + 2\ AlH_3 \rightarrow 2\ H_2AlCl + 2\ HZnCl \quad (5)$$

$$H_2AlCl + HZnCl \rightarrow ZnH_2 + HAlCl_2 \quad (6)$$

$$ZnH_2 + HZnCl \rightarrow H_3Zn_2Cl$$

$$2\ ZnCl_2 + 2\ AlH_3 \rightarrow H_3Zn_2Cl + H_2AlCl + HAlCl_2 \quad (7)$$

The infrared spectrum as well as the X-ray powder diffraction pattern of the solid product shows it to be a unique compound and not a physical mixture of zinc chloride and zinc hydride. The infrared spectra of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$, $ZnCl_2 \cdot 0.11\ Et_2O$ and $ZnCl_2$ in the solid state are reported in Figure 4 and the X-ray powder diffraction patterns are listed in Table 1.

In 2:1 mole ratio, zinc Chloride and AlH_3 reacted to yield the same solid compound, $H_3Zn_2Cl \cdot Et_2O$ which was characterized by the elemental analysis, X-ray powder diffraction and infrared analysis. However, the infrared spectrum and elemental analysis of the filtrate showed it to contain only aluminum chloride indicating the following sequence of reactions:

$$2\ ZnCl_2 + AlH_3 \rightarrow 2\ HZnCl + HAlCl_2 \quad (8)$$

$$HZnCl + HAlCl_2 \rightarrow ZnH_2 + AlCl_3 \quad (9)$$

$$ZnH_2 + HZnCl \rightarrow H_3ZnCl \quad (10)$$

$$2\ ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + AlCl_3 \quad (11)$$

The infrared spectrum and elemental analysis of the solid compound obtained by reacting zinc chloride and AlH_3 in 3:1 mole ratio showed the solid product to be $H_3Zn_2Cl \cdot Et_2O$; however, the filtrate contained 1 mole of aluminum chloride as well as 1 mole of unreacted $ZnCl_2$ as expected from the results expressed in equation 11.

$$3\ ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + ZnCl_2 + AlCl_3 \quad (12)$$

When zinc chloride and alane were allowed to react in 1:4 mole ratio, H_3Zn_2Cl was again obtained but the elemental analysis gave a molar ratio of H:Zn:Cl:Al = 1.91:1.00:0.430:0.07. The high hydrogen ratio indicates that in the presence of excess AlH_3 some HZnCl reacts further with AlH_3 to form ZnH_2 rather than complexes with the ZnH_2 already present to form H_3Zn_2Cl. Thus, the H_3Zn_2Cl that is found is formed in the presence of ZnH_2.

In order to varify the existence of HZnCl, zinc chloride and $HAlCl_2$ were allowed to react in 1:1 mole ratio in diethyl ether. In this case also a white solid corresponding to a molar ratio of H:Zn:Cl:Al = 1.40: 1.00:0.766:0.12 was obtained, suggesting the formation of H_3Zn_2Cl.

$$4\ ZnCl_2 + 4\ HAlCl_2 \rightarrow 4\ HZnCl + 4\ AlCl_3 \quad (13)$$

$$2\ HZnCl \rightarrow ZnH_2 + ZnCl_2 \quad (14)$$

$$HZnCl + ZnH_2 \rightarrow H_3Zn_2Cl \quad (15)$$

$$HZnCl \rightarrow 1/2\ ZnH_2 + 1/2\ ZnCl_2 \quad (16)$$

$$4\ ZnCl_2 + 4\ HAlCl_2 \rightarrow H_3Zn_2Cl + 1/2\ ZnH_2 + 3/2\ ZnCl_2 + 4\ AlCl_3 \quad (17)$$

The above sequence of reactions show that H_3Zn_2Cl is formed in the presence of 1/2 ZnH_2, thus leading to a high H:Zn ratio.

<u>$ZnBr_2$ and AlH_3.</u> Like zinc chloride, zinc bromide was also allowed to react with AlH_3 in 1:1 and 2:1 mole ratios in ether to yield a white solid closely corresponding to the empirical formula H_3Zn_2Br. However, H_3Zn_2Br appeared to be less stable than H_3Zn_2Cl since it decomposed quite rapidly when the mixture was stirred for the same period of time at room temperature producing a light grey solid. The light grey color is

presumably due to the formation of zinc metal. The reactions were in general comparable with the reaction of zinc chloride with AlH_3. X-ray powder diffraction patterns for $ZnBr_2$, $ZnBr_2 \cdot 0.28\ Et_2O$ and $H_3Zn_2Br \cdot 0.29\ Et_2O$ are listed in Table 1.

ZnI_2 and AlH_3. In 2:1 mole ratio, zinc iodide and AlH_3 in diethyl ether reacted to yield a white solid corresponding to the composition $ZnI_2 \cdot AlH_3 \cdot 1.79\ Et_2O$. Infrared analysis and X-ray powder diffraction of the solid compound showed it to be different from a physical mixture of ZnI_2 and AlH_3. The infrared spectrum as well as the elemental analysis of the filtrate did not show the presence of any hydridoaluminum halides. Similarly, when the reaction was carried out in 1:4 mole ratio ZnI_2: AlH_3, a white solid resulted having the same composition. An infrared spectrum of the filtrate showed absorption bands due to AlH_3 alone. Therefore, it is safe to conclude that zinc iodide and AlH_3 react to produce the most stable compound $ZnI_2 \cdot AlH_3 \cdot n\ Et_2O$.

$$ZnI_2 + AlH_3 \rightarrow ZnI_2 \cdot AlH_3 \qquad (18)$$

$CdBr_2$ and AlH_3. In 1:1 mole ratio, $CdBr_2$ and AlH_3 in diethyl ether were allowed to react at -40° to -30° for 40 hr with stirring to yield a slightly grey solid which gave a molar ratio of Cd:H:Br, 1.00: 1.00:1.143. The solid decomposed to Cd, H_2 and $CdBr_2$ slowly at -20° and more rapidly at room temperature. As reported earlier by Wiberg and Henle,[2] CdH_2 was also found to decompose at -20°. Therefore, although the elemental analysis of the solid compound suggests the formation of HCdBr compound, the possibility of a physical mixture of CdH_2 and $CdBr_2$ cannot be ruled out. Elemental analysis of the filtrate showed the presence of H_2AlBr which was also supported by an infrared spectrum which exhibited bands characteristic of H_2AlBr.

In order to establish the nature of the solid product as HCdBr (eq. 19) and not a mixture of $CdBr_2$ and CdH_2 (eq. 20), an attempt was made to react a mixture of $CdBr_2$ and H_2AlBr in diethyl ether in 1:1 ratio at -40°. If the reaction proceeded according to equation 20, then $CdBr_2$ is produced in the presence of H_2AlBr. Since it is possible that $CdBr_2$ is reduced in the presence of H_2AlBr (eq. 21), the presence of $HAlBr_2$ would indicate the presence of $CdBr_2$ in solution. If indeed this reaction occurs (eq. 21) this would indicate the absence of $CdBr_2$ in the reaction product of $CdBr_2$ and AlH_3, thus eleminating eq. 20 as the reaction course. Unfortunately, no reaction took place; thus, it is not

$$CdBr_2 + AlH_3 \rightarrow \underline{HCdBr} + H_2AlBr \qquad (19)$$

$$CdBr_2 + AlH_3 \rightarrow \underline{1/2\ CdH_2 + 1/2\ CdBr_2} + H_2AlBr \qquad (20)$$

$$CdBr_2 + H_2AlBr \rightarrow HCdBr + HAlBr_2 \qquad (21)$$

possible to tell whether the reaction product is HCdBr or a physical mixture of CdBr and CdH_2.

Because of the low solubility of $CdBr_2$ in diethyl ether, an attempt was also made to study the reaction in THF; however, the reaction was found to be too slow at -40 to -30° and the reaction product decomposed above -20°.

CuCl and AlH_3. When cuprous chloride and AlH_3 were allowed to react in 1:1 mole ratio in ether at -76° and then allowed to warm slowly to room temperature, the reaction mixture turned completely black giving off a gas. The elemental analysis as well as an infrared spectrum of the filtrate suggests that the reaction takes place according to the followiong reaction sequence:

$$CuCl + AlH_3 \rightarrow CuH + H_2AlCl \quad (22)$$

$$CuCl + H_2AlCl \rightarrow CuH + HAlCl_2 \quad (23)$$

$$CuH + AlH_3 \rightarrow CuAlH_4 \quad (24)$$

$$2\ CuCl + 2\ AlH_3 \rightarrow CuH + CuAlH_4 + HAlCl_2 \quad (25)$$

The infrared spectrum of the filtrate showed a sharp band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1}. Elemental analysis of the filtrate indicated only 43% of the total aluminum. The infrared spectrum of the black solid product did not show any absorption bands due to either hydridoaluminum compounds or hydridocopper compounds. Thus, it appears that the black solid product is a mixture of copper and aluminum metal formed according to equation 26. Since the filtrate was shown to be an

$$CuH + CuAlH_4 \rightarrow 2\ Cu + Al + 5/6\ H_2 \quad (26)$$

ether solution of $HAlCl_2$ and since half of the aluminum was in the filtrate and half in the precipitate, it appears that there is ample data to suggest the above reaction sequence.

Table 1. X-Ray Powder Pattern d-Spacing Data

$MgBr_2 \cdot 0.24Et_2O$		$MgBr_2 + AlH_3 \cdot 1.4Et_2O$		$MgBr_2 + 2\ AlH_3$	
d,A	I/I_0	d,A	I/I_0	d,A	I/I_C
8.0	s	9.25	s	6.2	vw
7.25	s	8.0	s	4.20	s
6.30	m	7.25	s	4.05	w
5.90	m	5.60	vw	3.65	m
5.4	w	5.30	w	3.08	m
5.0	w	3.95	vw	2.95	m
4.60	m	3.75	w	2.77	w
3.6	m,br	3.50	s	2.70	s
3.39	w	3.23	s	2.325	s
3.25	w	2.95	m	2.02	s
3.15	m	2.72	m	1.90	w
3.05	s	2.70	w	1.425	s
2.95	s	2.50	m	1.215	s
2.85	s	2.40	w	1.165	w
2.74	m	2.325	m		
2.64	m	2.24	vw		
2.36	s	2.125	w		
1.98	m,br	2.02	w		
1.81	s	1.90	w		
1.87	w	1.60	w		
1.83	w	1.425	w		
1.77	w	1.215	w		
1.72	m				
1.66	m				
1.630	m				
1.615	m				
1.46	vvw				
1.345	vvw				
1.255	vvw				

Table 1 Continued

ZnH_2		$ZnCl_2$		$ZnCl_2 \cdot 0.11Et_2O$		$H_3Zn_2Cl \cdot 0.20Et_2O$	
d,A	I/I_0	d,A	I/I_0	d,A	I/I_0	d,A	I/I_0
4.51	vw	4.85	s	6.85	m	7.8	s
4.23	s	4.70	s	5.50	m	5.80	w
3.80	vw	3.80	w	4.80	s	5.40	w
3.40	m	3.26	m	4.50	m	4.0	m
2.97	vw	3.19	m	3.80	vw	3.55	w
2.82	vw	3.02	s	3.55	m	3.15	w
2.608	w	2.87	s	3.42	w	2.75	s
2.468	vw	2.85	w	3.30	w	2.65	s
2.387	m	2.35	w	3.05	s	2.37	m
2.290	m	2.22	w	2.87	m	2.00	w
2.225	m	2.12	vw	2.57	w	1.79	vw
2.135	w	1.960	vw	2.35	m	1.69	w
2.085	w	1.920	m	2.20	m	1.58	m
2.017	vw	1.860	s	2.06	w	1.55	w
1.905	w	1.730	s	1.97	w	1.51	w
1.764	w	1.620	w	1.95	m		
1.688	vw	1.592	s	1.865	s		
1.630	vw	1.490	w	1.730	m		
1.562	vw	1.455	w	1.620	m		
1.486	vw	1.280	vw	1.590	w		
1.464	vw	1.265	vw	1.570	m		
1.416	vw	1.145	vw	1.485	vw		
		1.350	vw	1.350	vw		
		1.265	vw	1.265	vw		
		1.215	vw	1.215	vw		
		1.095	vw	1.095	vw		

Table 1 Continued

$ZnBr_2 \cdot 0.285Et_2O$		$H_3Zn_2Br \cdot 0.29Et_2O$	
d,A	I/I_0	d,A[+]	I/I_0
6.5	vvw	10.0	w,br
4.2	w	3.5	w,br
3.4	s		
2.80	vvw		
2.55	vw		
1.99	m		
1.95	s		
1.70	m		
1.64	w		
1.27	w		
1.150	vw		

$AlH_3 \cdot 0.25Et_2O$		ZnI_2		$ZnI_2 \cdot 0.35Et_2O$		$ZnI_2AlH_3 \cdot 0.192\ Et_2O$	
d,A	I/I_0	d,A	I/I_0	d,A	I/I_0	d,A	I/I_0
11.5	s	3.45	s	3.45	s	8.80	m
4.55	m	3.05	w	3.05	vw	7.00	m
3.85	m	2.17	w	2.17	vw	5.40	vw
2.85	m	2.12	m	2.12	m	4.90	w
2.32	m	1.84	m	1.84	m	4.35	w
		1.78	w	1.78	w	3.95	w
		1.37	vw	1.375	vw	3.4	s
		1.235	vw	1.245	vw		

[+]Powder diffraction lines were obtained as two broad halos and these are only approximate distances.

Table II. Electronegativities of Elements and Electronegativity Difference Between the Metal and Halogen.

Elements	Electronegativity	Metal Halide	Electronegativity Difference
Ca	1.04	$CaBr_2$	1.87
Mg	1.23	$MgBr_2$	1.64
Be	1.47	$BeCl_2$	1.56
Al	1.47	$AlCl_3$	1.55
Zn	1.66	$ZnCl_2$	1.47
Cd	1.70	$AlBr_3$	1.35
Cu	1.90	$ZnBr_2$	1.30
H	2.20	$CdBr_2$	1.27
I	2.5	CuCl	1.18
Br	2.8	AlI_3	1.04
Cl	3.0	ZnI_2	1.04

Figure I. Infrared study of the Reaction of AlH_3 with $AlCl_3$ in diethyl ether. 1. AlH_3 2. AlH_2Cl 3. $AlHCl_2$

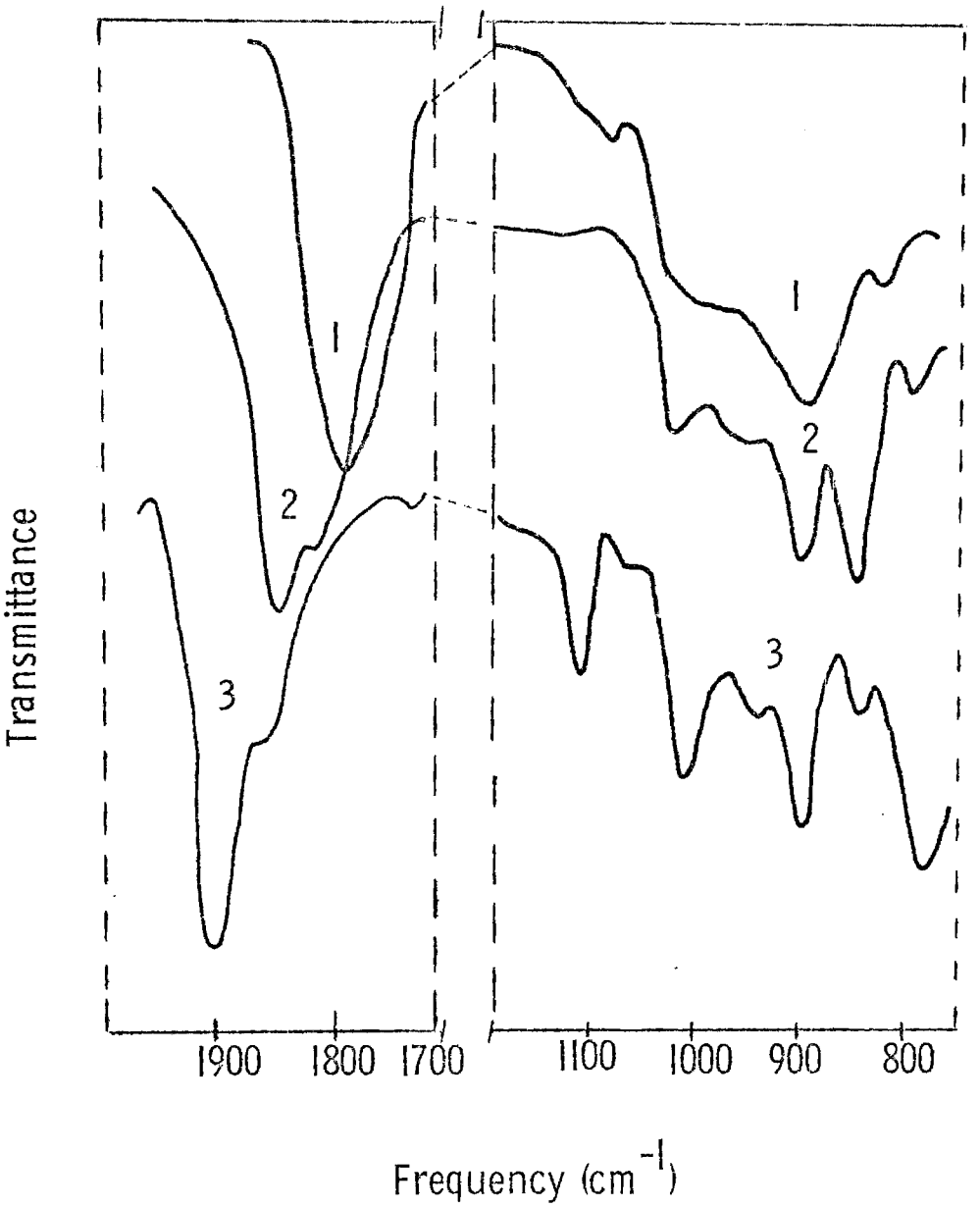

Transmittance
1
2
3
1
2
3
1900
1800
1700
1100
1000
900
800
Frequency (cm^{-1})

Figure 2. Infrared spectra of AlH_3, H_2AlBr and $HAlBr_2$ in diethyl ether

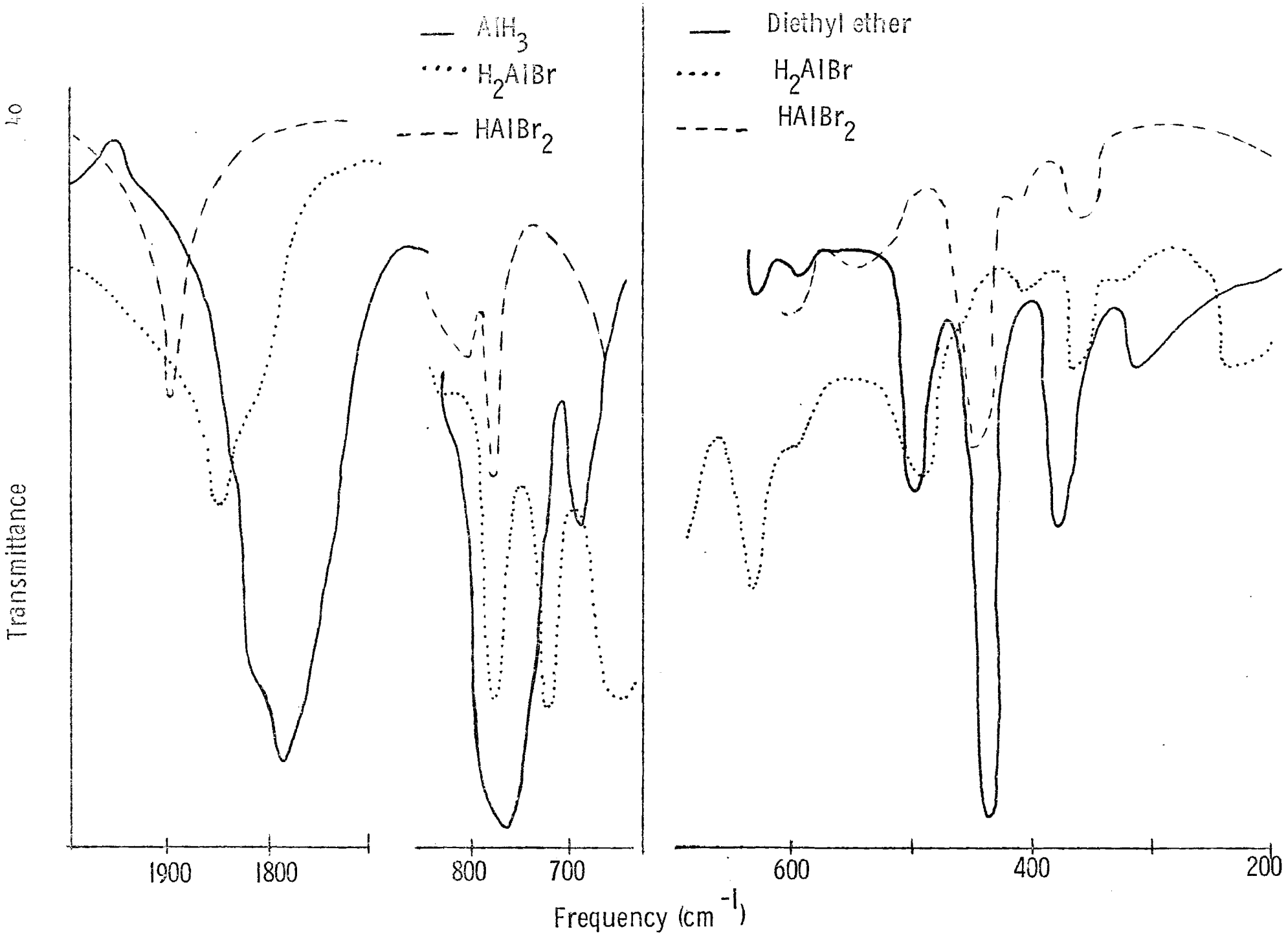

AlH3
H2AlBr
HAlBr2
Diethyl ether
H2AlBr
HAlBr2
Transmittance
1900
1800
800
700
600
400
200
Frequency (cm -1)

Figure 3. Infrared spectra of (a) the reaction product of $MgBr_2 + AlH_3$ (——) and (b) $MgBr_2 \cdot n(C_2H_5)_2O$ (• • • •).

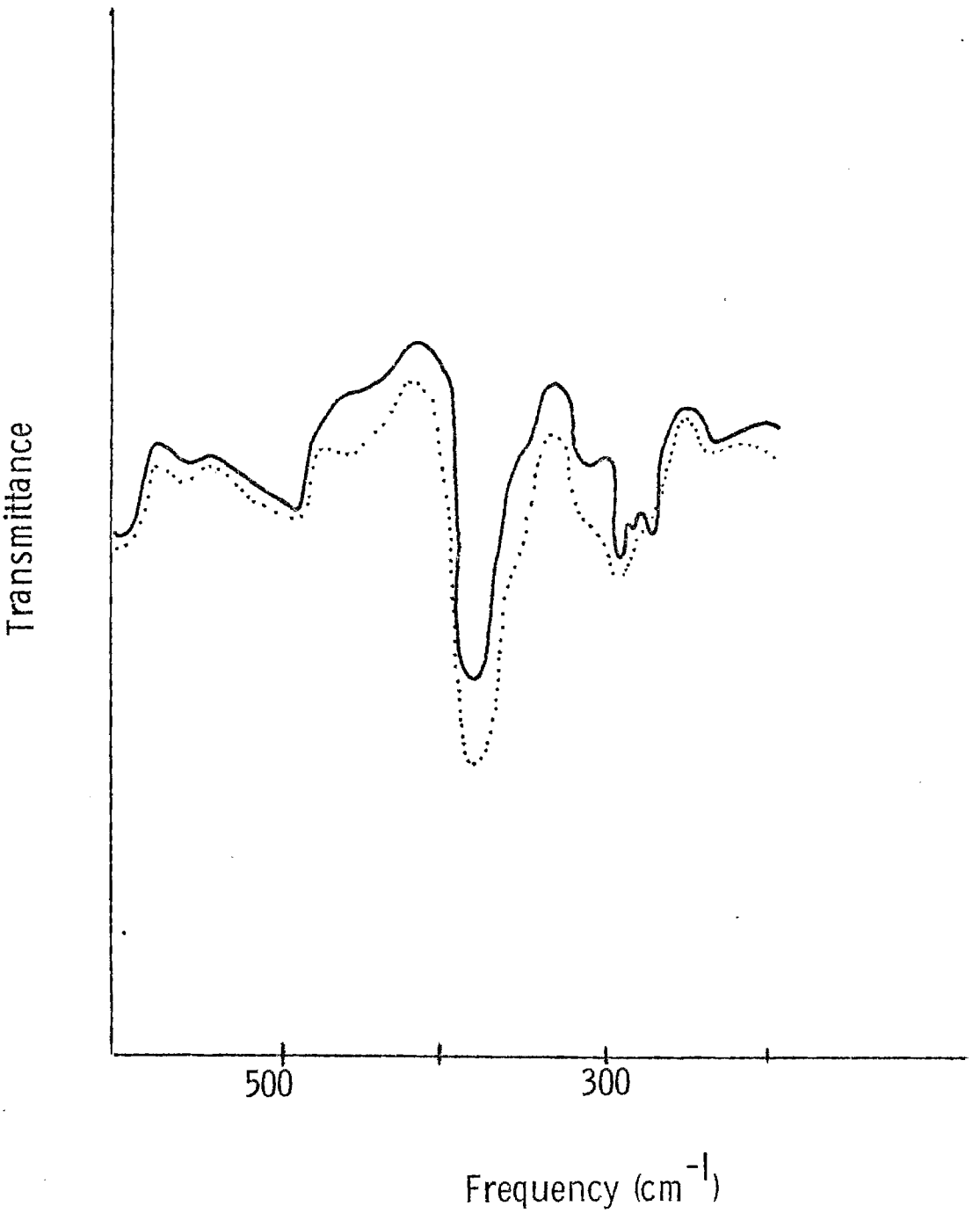

Transmittance
500
300
Frequency (cm^{-1})

Figure 4. Infrared spectra of (a) $ZnCl_2$ (• • • •)
(b) $ZnCl_2 \cdot 0.11Et_2O$ (– – –) and (c) H_3Zn_2Cl (——).

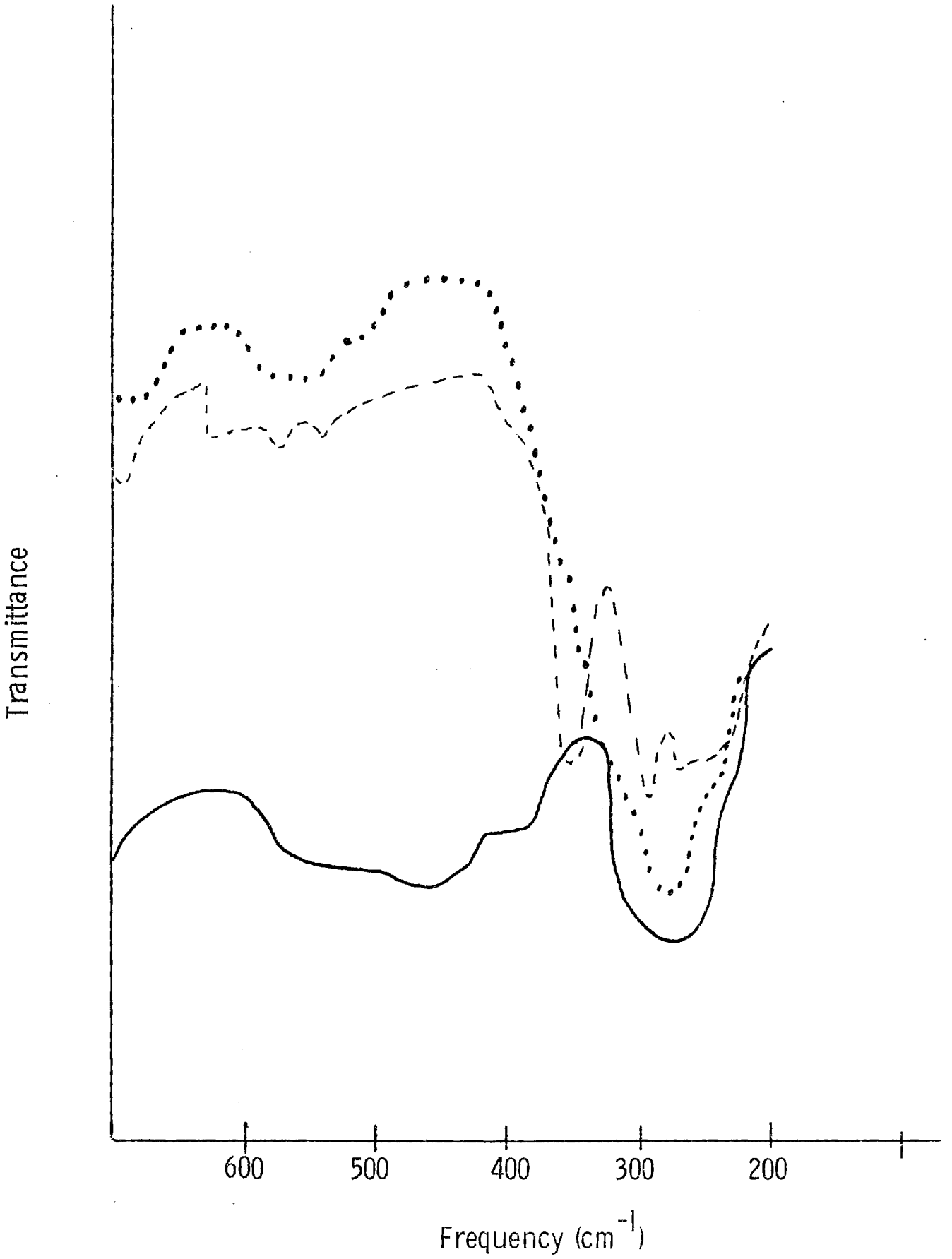
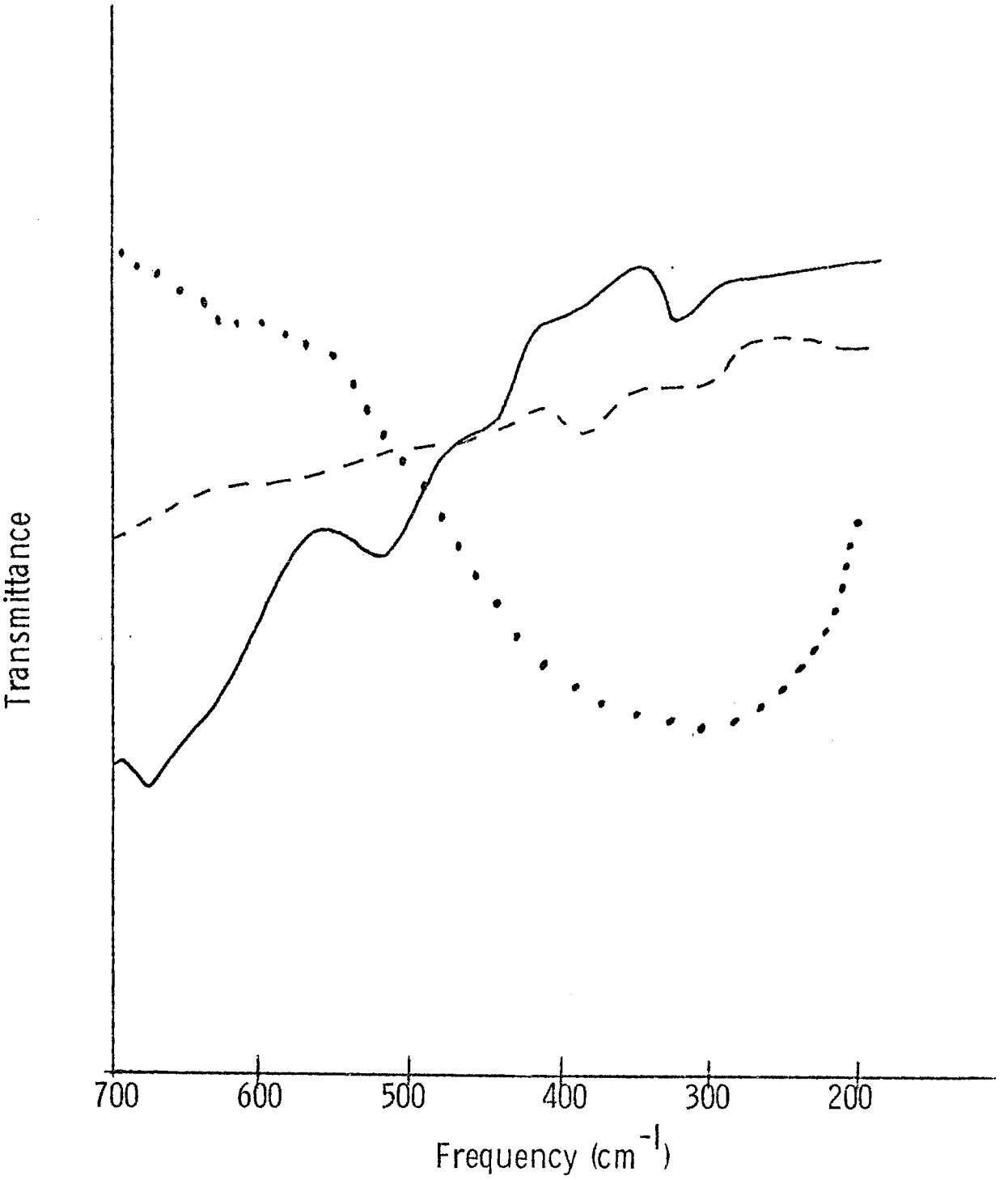

Transmittance
600
500
400
300
200
Frequency (cm^{-1})

Figure 5. Infrared spectra of (a) ZnI_2 (• • •), (b) $ZnI_2 \cdot 0.35Et_2O$ (– –) and (c) $ZnI_2 \cdot AlH_3$ (——).


Transmittance
700
600
500
400
300
200
Frequency (cm^{-1})

Attempted Desolvation of Ether Soluble AlH_3

The AlH_3 produced by the reaction of $LiAlH_4$ and $BeCl_2$ in ether shows different physical properties than the product prepared from $LiAlH_4$ and $AlCl_3$. We therefore thought that ether free AlH_3 might be produced from this product more easily than AlH_3 produced by other methods.

The ether solvent from an etheral solution of AlH_3 was removed under vacuum and the resulting white solid was heated to 60° for 6 hr. At the end of this time the sample was analysed and could be represented by the formula $AlH_3 \cdot 0.25Et_2O$. The sample was heated to 70° overnight and at the end of this time a grey solid resulted which gave an Al:H ratio of 1.0:1.78.

In a separate experiment the ether was removed from a solution of AlH_3 and the solid subjected to vacuum for 1 week. At the end of this time analysis of the sample indicated that the solid was $AlH_3 \cdot 0.25Et_2O$. The sample was again evacuated and placed in an oil bath (pre-heated to 75°) for 1 hour. Analysis of the sample after 1 hr. gave an Al:H ratio of 1.0:2.97, Al Found: 70%. Anal. Calcd. for AlH_3: 89.99%; $AlH_3 \cdot 0.25Et_2O$, 55%. The sample was placed in the oil bath (at 75°) for another 30 min. Analysis of the sample after this time gave an Al:H ratio of 1.0:0.5.

In conclusion, we would like to point out that although the ether to Al ratio in $AlH_3 \cdot 0.25$ ether could be lowered by heating the sample for short periods of time in a vacuum, we were not successful in removing all the ether without decomposing the sample.

Reactions of $MZn_x(CH_3)_{2x}H$ Compounds with Aluminum Hydride. Concerning the Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc.

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Abstract

When AlH_3 was allowed to react with $LiZnMe_2H$, $LiZn_2Me_4H$, and $NaZn_2Me_4H$ in tetrahydrofuran in a 1:1 molar ratio, $LiZnMe_2AlH_4$, $LiZn_2Me_4AlH_4$, and $NaZn_2Me_4AlH_4$ were formed. $LiZn_2Me_4AlH_4$ and $LiZnMe_2AlH_4$ are also formed in the reaction of dimethylzinc with $LiAlH_4$ in tetrahydrofuran in 2:1 and 1:1 molar ratios. Likewise, $NaZn_2Me_4AlH_4$ and $NaZn(CH_3)_2AlH_4$ were also formed in the reaction of dimethylzinc with $NaAlH_4$ in tetrahydrofuran in 2:1 and 1:1 molar ratios.

The mechanism of formation of KZn_2H_5 or $NaZn_2H_5$ from the reaction of AlH_3 with $KZnMe_2H$ or $NaZnMe_2H$ is discussed. The mechanism of formation of KZn_2H_5 from the reaction of $KZn_2(CH_3)_4H$ with AlH_3 and the formation of ZnH_2 by reaction of dimethylzinc with tetrahydroaluminates is also discussed.

Introduction

Recently we have reported the synthesis of nine complex metal hydrides of zinc[1,2,3] -Li_3ZnH_5, Li_2ZnH_4, $LiZnH_3$, Na_2ZnH_4, $NaZnH_3$,[4] $NaZn_2H_5$, K_2ZnH_4, $KZnH_3$, and KZn_2H_5. All but two of these complex metal

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(1) E. C. Ashby and R. G. Beach, Inorg. Chem., 10, 2486 (1971). (2) E. C. Ashby and John Watkins, Chem. Comm., 998, (1972). (3) E. C. Ashby and John J. Watkins, Inorg. Chem., 12, 2493 (1973). (4) This compound was first prepared by Shriver and co-workers. D. J. Shriver, G. J. Kubas, and J. A. Marshall, J.A.C.S., 93, 5067, (1971).

hydrides were prepared by the reaction of an aluminohydride, $LiAlH_4$, $NaAlH_4$, or AlH_3, with an ate complex of zinc. Li_3ZnH_5, Li_2ZnH_4, and $LiZnH_3$ were prepared by the reaction of the corresponding ate complexes: $Li_3Zn(CH_3)_5$, $Li_2Zn(CH_3)_4$, and $LiZn(CH_3)_3$ with $LiAlH_4$ in diethyl ether.[2,3] $NaZnH_3$ was obtained from the reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in tetrahydrofuran; and $KZnH_3$ was prepared by the reaction of $KZn(CH_3)_2H$ with $LiAlH_4$ in tetrahydrofuran.[3] Quite surprisingly $NaZn_2H_5$ and KZn_2H_5 were produced by the reactions of AlH_3 with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in tetrahydrofuran.[3] An obvious extension of this work would be to prepare $LiZn_2H_5$ by reacting $LiZn(CH_3)_2H$ with AlH_3, however, this reaction yielded the THF soluble complex $LiZn(CH_3)_2AlH_4$ instead. The latter complex can also be prepared by reacting $LiAlH_4$ with $(CH_3)_2Zn$ in a 1:1 molar ratio in THF. The complex $LiZn_2(CH_3)_4AlH_4$ can be prepared by reacting $LiAlH_4$ with $(CH_3)_2Zn$ in a 1:2 molar ratio in THF or by reacting $LiZn_2(CH_3)_4H$ with AlH_3 in THF. In a similar way $NaZn_2(CH_3)_4AlH_4$ can be prepared either by reacting $NaAlH_4$ with $(CH_3)_2Zn$ in a 1:2 molar ratio in THF or by reacting $NaZn_2(CH_3)_4H$ with AlH_3 in THF.

$LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4AlH_4$, and $NaZn_2(CH_3)_4AlH_4$ are the first trimetal complexes between an alkali metal, zinc, and aluminum to be reported. The structures of these complexes can be determined by examination of their infrared spectra. A knowledge of the structures of these complexes, coupled with the fact that they can be prepared by reacting $MAlH_4$ with $(CH_3)_2Zn$ in THF offers the first view of what could be the intermediate involved in the formation of ZnH_2 from $(CH_3)_2Zn$ and $LiAlH_4$, a reaction known to proceed in diethyl ether.[5]

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(5) G. D. Barbaras, C. Dillard, A. E. Finholt, J. Wartik, K. E. Wilzbach, and H. D.Schlesinger, J. Amer. Chem. Soc., 73, 4585 (1951).

Since our discovery of the use of aluminohydrides in the synthesis of main group complex metal hydrides,[2,3] we have been very interested in the nature of exchange reactions between Al-H species and main group alkyl metal species. We feel that, in addition to providing a route to trimetal hydrides, an in depth study of the formation of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ could provide insight into the nature of exchange reactions between $LiAlH_4$, $NaAlH_4$, or AlH_3 and the ate complexes of zinc used to prepare the complex metal hydrides of zinc cited earlier. It is the purpose of this paper to discuss the mechanisms by which some of the complex metal hydrides of zinc are formed.

Experimental

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[6] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system.[7]

(6) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(7) E. C. Ashby and R.D. Schwartz, J. Chem. Ed., 51, 65(1974).

Infrared spectra were obtained using a Perkin Elmer 621 Spectrophotometer. Solutions were run in matched 0.10 mm pathlength NaCl cells. X-ray powder data were obtained on a Phillip-Norelcc X-ray unit using a 114.6 mm camera with nickel filtered CuK_α radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hours. D-spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually.

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Methane in the presence of hydrogen was determined in a transimeter. Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration. Halogens were determined by the Volhard procedure.

Materials. Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of t-butyllithium at 4000 psig for 24 hours. Solutions of lithium and sodium aluminum hydride (Ventron, Metal Hydride Division) were prepared in both diethyl ether and tetrahydrofuran in the usual manner. Dimethyl- and di-s-butylzinc were prepared by the procedure of Noller.[8] Methyl and s-butyl iodides were obtained from Fisher Scientific.

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(8) C. R. Noller, Org. Syn., 12, 86 (1932).

The iodides were dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc-copper couple was obtained from Alfa Inorganics. The reactions of zinc-copper couple with methyl iodide were allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture under nitrogen. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher Reagent) over lithium aluminum hydride. Ultra-pure hydrogen (99.9995%) obtained from the Matheson Corporation was used for hydrogenation experiments. Aluminum hydride was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF.

Li_2SO_4 was removed by filtration and a lithium free solution of AlH_3 in THF was obtained.[9]

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(9) H. C. Brown and N. M. Yoon, J. Amer. Chem. Soc., 88, 1464 (1966).

Reaction of AlH_3 with $LiZn(CH_3)_2H$ in Tetrahydrofuran. 5 mmoles of dimethylzinc in tetrahydrofuran was added to 5 mmoles of a lithium hydride slurry in tetrahydrofuran. This mixture was stirred until all the lithium hydride dissolved (forming $LiZn(CH_3)_2H$), then 5 mmoles of AlH_3 in THF was added. No precipitate formed. After one hour stirring the clear solution still remained. At this time another 5 mmoles of AlH_3 was added. A white precipitate appeared immediately. This slurry was stirred for one hour and filtered. The solid, which was dried under vacuum at room temperature, had a molar ratio of Zn:H of 1.00:2.04. Very little lithium or aluminum was found in the solid.

Elemental analysis and X-ray powder diffraction and vacuum DTA-TGA data confirmed that the solid was ZnH_2. The filtrate contained 9.09 mmoles of aluminum, 0.199 mmoles of zinc, and 4.80 mmoles of lithium. These results indicate the initial formation of some type of complex between AlH_3 and $LiZn(CH_3)_2H$ which was destroyed by the addition of excess AlH_3.

Reaction of AlH_3 with $LiZn_2(CH_3)_4H$ in Tetrahydrofuran. 8.35 mmoles of dimethylzinc in tetrahydrofuran were added to 4.18 mmoles of LiH slurried in tetrahydrofuran. A clear solution resulted to which was added 4.17 mmoles of AlH_3 in tetrahydrofuran. The mixture still remained clear, even after one hour stirring. An additional 4.17 mmoles of AlH_3 was then added to the mixture. A white precipitate appeared immediately.

This slurry was stirred one hour and filtered. The solid, which was dried under vacuum at room temperature, contained Zn:H in a molar ratio of 1.00:2.08, with very little aluminum or lithium. An X-ray powder diffraction pattern of the solid showed it to be ZnH_2. The filtrate contained 8.08 mmoles of aluminum, 4.18 mmoles of lithium, and 0.42 mmoles of zinc in a molar ratio of 1.93:1.00:0.099. An infrared spectrum of the filtrate contained two bands in the Al-H stretching region. One was centered at 1750 cm^{-1} and corresponded to $Al(CH_3)_2H$; the other was centered at 1660 cm^{-1} and corresponded to $LiAl(CH_3)_2H_2$. Infrared spectra confirm the existence of complexes between $LiZn_2(CH_3)_4H$ or $LiZn(CH_3)_2H$ and AlH_3. Unfortunately both complexes decompose on standing at room temperature.

Reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in Tetrahydrofuran at Molar Ratios of 1:2, 2:3, and 1:1. To 10 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added (1) 5 mmoles of a 0.386 M solution of $LiAlH_4$ in THF, (2) 2.5 mmoles of a 0.386 M solution of $LiAlH_4$ in THF, and (3) 2.5 mmoles of a 0.386 M solution of $LiAlH_4$ in THF, so that after the first addition of the ratio of Al:Zn would be 1:2, after the second 2:3, and after the third 1:1. No precipitate of ZnH_2 formed in any of the reactions. After each addition the mixture was stirred for about 15 minutes, and an infrared spectrum run on the clear solution. The infrared spectra, shown in Figure 3, correspond to the spectra observed for $LiZn_2Me_4AlH_4$ (1:2 ratio of Al:Zn) and $LiZnMe_2AlH_4$ (1:1 ratio of Al:Zn).

Reaction of $(CH_3)_2Zn$ with $LiAlH_4$ in Tetrahydrofuran at Molar Ratios of 1:1 and 2:1 (inverse addition). To 10 mmoles of a 0.386 M solution of $LiAlH_4$ in THF was added 20 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF in 10 mmole increments. No precipitate of ZnH_2 formed

after either incremental addition. After each addition, the mixture was stirred for about 15 minutes and an infrared spectrum run on the clear solution. The infrared spectra, shown in Figure 4, corresponded to the spectra observed for $LiZnMe_2AlH_4$ and $LiZn_2Me_4AlH_4$.

Reaction of $NaZn(CH_3)_2H$ with AlH_3 in Tetrahydrofuran. 5 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added to 5 mmoles of NaH slurried in THF. A clear solution of $NaZn(CH_3)_2H$ formed. Now 5 mmoles of a 0.1025 M solution of AlH_3 in THF was added. An off white precipitate appeared immediately. Infrared spectra were run on the $(CH_3)_2Zn$ solution, the $NaZnMe_2H$ solution, and the supernatent left after 5 minutes and 24 hours after AlH_3 was added to the $NaZn(CH_3)_2H$ solution. After sitting one day the precipitate was filtered. The ratio of Na:Zn:H in the solid was 1.02:2.00:4.86 and an X-ray powder diffraction pattern showed it to be $NaZn_2H_5$. The filtrate contained Na, Al, and Zn in molar ratios of 1.03:2.00:0.061. The infrared spectra are shown in Figure 5.

Reaction of $NaZn_2(CH_3)_4H$ with AlH_3 in Tetrahydrofuran. 10 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added to 5 mmoles of NaH slurried in THF, followed by 5 mmoles of a 0.557 M solution of AlH_3 in THF. A clear solution resulted which was believed to be $NaZn_2(CH_3)_4AlH_4$. Infrared spectra were run on the $(CH_3)_2Zn$ solution, the $NaZn_2(CH_3)_4H$ solution, and the adduct between $NaZn_2(CH_3)_4H$ and AlH_3. To the 5 mmoles of $NaZn_2(CH_3)_4AlH_4$ was added 5 mmoles of AlH_3 in THF. A white precipitate formed immediately. This mixture was stirred about one hour, the precipitate was allowed to settle, and an infrared spectrum run on the supernatent. Next the mixture was filtered. The solid was shown by powder pattern analysis to be ZnH_2 and the molar ratio of Na:Al:Zn in the filtrate was 1.01:2.00:0.18. The infrared spectra are shown in Figure 6.

Reaction of $(CH_3)_2Zn$ with $NaAlH_4$ in Tetrahydrofuran at Molar Ratios of 1:1 and 2:1. To 10 mmoles of a 0.813 M solution of $NaAlH_4$ in THF was added 20 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF in 10 mmole increments. When 10 mmoles of $(CH_3)_2Zn$ had been added an off white precipitate formed. When the second 10 mmoles of $(CH_3)_2Zn$ was added, the entire precipitate redissolved and a clear solution formed. After each of the additions the solution or mixture was stirred for 15 minutes and an infrared spectrum run on the solution or supernatent. The infrared spectra, shown in Figure 7, corresponded to $NaZn_2(CH_3)_4AlH_4$ when the ratio of Al:Zn was 1:2 and $NaZn(CH_3)_2AlH_4$ when the ratio of Al:Zn was 1:1.

Reaction of $NaAlH_4$ with $(CH_3)_2Zn$ in Tetrahydrofuran at Molar Ratios of 1:2, 3:4 and 1:1 (inverse addition). To 10 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added (1) 5 mmoles of a 0.813 M solution of $NaAlH_4$ in THF, (2) 2.5 mmoles of a 0.813 M solution of $NaAlH_4$ in THF, and (3) 2.5 mmoles of a 0.813 M solution of $NaAlH_4$ in THF in three separate increments. No precipitate formed until the ratio of Al:Zn was 1:1. In the first two cases, the solutions were stirred 15 minutes and then infrared spectra run on the resulting solutions. In case three an infrared spectrum was run on the supernatent 5 minutes, 2.5 hours, 28 hours, 4 days and 7 days after the initial addition. The infrared spectra are shown in Figure 8.

Reaction of $NaAlH_4$ with $(CH_3)_2Zn$ in a 1:1 Molar Ratio. 10 mmoles of a 0.921 M solution of $(CH_3)_2Zn$ in THF was added to 10 mmoles of a 0.813 M solution of $NaAlH_4$ in THF. Initially a white precipitate appeared, but it quickly disappeared and an off white precipitate appeared. The

mixture was stirred for about three hours and filtered. The solid contained Na:Zn:H in a molar ratio of 1.00:2.00:4.87. An X-ray powder diffraction pattern showed the solid to be $NaZn_2H_5$. The molar ratio of Na:Al:Zn in the filtrate was 1.75:2.00:1.38. An infrared spectrum of the filtrate showed the presence of $NaZn(CH_3)_2AlH_4$. After sitting about 9 days, more solid appeared from the filtrate. This mixture was refiltered. The molar ratio of Na:Al:Zn in the filtrate was now 1.05:2.00:0.13. An infrared spectrum of the filtrate now corresponded to $NaAl_2Me_4H_3$, the same product formed in the reaction of $NaZn(CH_3)_2H$ with AlH_3.

Reaction of AlH_3 with $(CH_3)_2Zn$ in Tetrahydrofuran. 5 mmoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added to 5 mmoles of a 0.555 M solution of AlH_3 in THF. A white precipitate formed immediately. The mixture was stirred about one hour and filtered. The ratio of Zn:H in the solid was 1.00:2.03 and an X-ray powder pattern showed it to be ZnH_2. No zinc remained in the filtrate. An infrared spectrum of the filtrate showed it to be $Al(CH_3)_2H$.

Reaction of ZnH_2 with $NaAl(CH_3)_2H_2$ in Tetrahydrofuran. 2.5 mmoles of ZnH_2 slurried in THF was added to 2.5 mmoles of $NaAl(CH_3)_2H_2$ in THF. All the ZnH_2 dissolved in less than a minute and a clear solution formed. An infrared spectrum was run on this clear solution and it corresponded to $NaZnMe_2AlH_4$. After about 20 minutes an off white precipitate began to appear. This mixture was stirred for a day and filtered. The solid contained Na:Zn:H in a molar ratio of 1.06:2.00:4.81 and an X-ray powder pattern showed it to be $NaZn_2H_5$. The filtrate was allowed to stand another week. After this time more solid appeared. The mixture was refiltered. The molar ratio of Na:Zn in the solid was 1.05:2.00. The molar ratio of Na:Al:Zn in the filtrate was now 1.03:2.00:0.17. An

infrared spectrum of the filtrate corresponded to $NaAl_2Me_4H_3$.

Preparation of $KAlH_4$. 10 mmoles of KH slurried in THF were added to 10 mmoles of a 0.1025 M solution of AlH_3 in THF. The mixture was stirred for a few days, then a sample of the solid isolated and analyzed. The molar ratio of K:Al:H in the solid was 1.03:1.00:3.91. The $KAlH_4$ was stored under THF and used as a slurry.

Reaction of $KZn(CH_3)_2H$ with AlH_3 in Tetrahydrofuran. 5 mmoles of KH slurried in THF was added to 5 mmoles of $(CH_3)_2Zn$ in THF. An infrared spectrum was run on the solution formed. Next 5 mmoles of a 0.1025 M solution of AlH_3 in THF was added to the solution of $KZn(CH_3)_2H$. As quickly as possible an infrared spectrum was run on the supernatent hoping to see the spectrum of the intermediate which leads to the products KZn_2H_5 and $KAl_2(CH_3)_4H_3$. The spectra are shown in Figure 9.

Reaction of $KAlH_4$ with $(CH_3)_2Zn$ in Tetrahydrofuran in 1:1 Molar Ratio. 2.5 mmoles of a 0.921 M solution of $(CH_3)_2Zn$ in THF was added to 2.5 mmoles of $KAlH_4$ slurried in THF. The mixture was stirred for 30 minutes, a solid remained throughout, and an infrared spectrum run on the supernatent. The spectrum is shown in Figure 9. After about two hours the mixture was filtered. The solid contained K:Zn:H in a molar ratio of 0.99:2.00:4.92. The X-ray powder diffraction pattern of the solid showed it to be KZn_2H_5. The ratio of K:Al:Zn in the filtrate was 1.01:2.00:0.00.

Reaction of $KAlH_4$ with $(CH_3)_2Zn$ in Tetrahydrofuran in a 1:2 Molar Ratio. 5 mmoles of a 0.921 M solution of $(CH_3)_2Zn$ in THF was added to 2.5 mmoles of $KAlH_4$ slurried in THF. A clear solution formed within seconds. As quickly as possible an infrared spectrum was run on this solution. After 10 minutes a white solid began to appear. The mixture was stirred for four

hours then filtered. The solid contained K:Zn:H in a molar ratio of 1.02:2.00:4.87. An X-ray powder diffraction pattern of the solid showed it to be KZn_2H_5. The molar ratio of K:Zn:Al in the filtrate was 1.01: 2.00:5.09. An infrared spectrum was run on the filtrate. All spectra are shown in Figure 10.

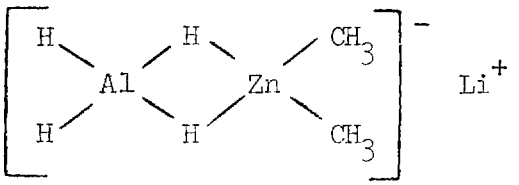
Reaction of $KZn_2(CH_3)_4H$ with AlH_3 in Tetrahydrofuran at Molar Ratios of 2:1, 1:1, and 1:2. 2.5 mmoles of KH slurried in THF was added to 5 mmoles of a 0.921 M solution of $(CH_3)_2Zn$ in THF. After the solution turned clear, marking the formation of $KZn_2(CH_3)_4H$, 1.25 mmoles of a 0.1025 M solution of AlH_3 in THF was added. The resulting clear solution was stirred 15 minutes then an infrared spectrum run. 1.25 mmoles of a 0.1025 M solution of AlH_3 in THF was added to this solution which still was clear. A white precipitate began forming immediately. An infrared spectrum was run on the supernatent. Next, another 2.5 mmoles of AlH_3 were added. The mixture was stirred 15 minutes, then another infrared spectrum run, and finally the mixture was filtered. The solid contained K:Zn:H in a molar ratio of 1.02:2.00:4.85, and an X-ray powder diffraction pattern showed it to be KZn_2H_5. The infrared spectrum showed the filtrate to be $(CH_3)_2AlH$. All spectra are shown in Figure 10.

In a separate experiment, 2.5 mmoles of AlH_3 in THF was added to 2.5 mmoles of $KZn_2(CH_3)_4H$ in THF. The resulting slurry was stirred for 4 hours then filtered. The solid contained K:Zn:H in a molar ratio of 1.06:2.00:4.91. An X-ray powder diffraction pattern showed the solid to be KZn_2H_5. The molar ratio of K:Zn:Al in the filtrate was 1.02:2.00:5.05.

Results and Discussion

The Reactions Between $MZn(CH_3)_2H$ or $MZn_2(CH_3)_4H$ and Alane. When AlH_3 was added to $LiZn(CH_3)_2H$ in an attempt to prepare $LiZn_2H_5$, quite a strange

thing happened. The reaction yielded no precipitate, only a clear solution. This behavior indicates the formation of some type of stable complex between AlH_3 and $LiZn(CH_3)_2H$. Information concerning this complex was obtained by examining its infrared spectrum (shown in Figure I). There is a strong, broad band in the terminal Al-H stretching region centered at 1660 cm^{-1}. The terminal Al-H stretching vibration for AlH_3 and $LiAlH_4$ in THF occurs at 1750 and 1691 cm^{-1}, respectively. Neither one of these absorptions correspond to the observed band. The Al-H stretching vibration for $LiAl(CH_3)_2H_2$ in THF occurs about 1660 cm^{-1}; however, in order for $LiAl(CH_3)_2H_2$ to be present in solution, methyl-hydrogen exchange involving CH_3-Zn and Al-H to Zn-H and Al-CH_3 would have had to occur. Such exchange would have surely resulted in the precipitation of ZnH_2. Since no precipitate was observed and since the Zn-CH_3 stretching vibration at 690 cm^{-1} was still present in the spectrum, the existence of $LiAl(CH_3)_2H_2$ is doubtful. The suggestion at this point, is that $LiZn(CH_3)_2H$ and AlH_3 form a stable complex in THF. A tentative structure for this complex is shown below.



$(LiZn(CH_3)_2AlH_4)$

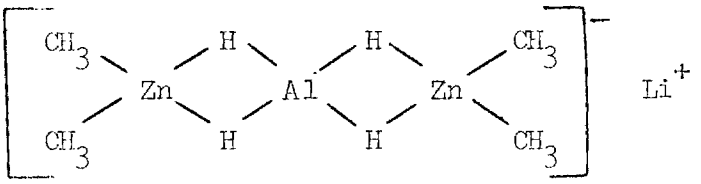
The remainder of the bands in the infrared spectrum of $LiZn(CH_3)_2AlH_4$ are given in Table I. It is interesting to note that on formation of the "ate" complex $LiZn(CH_3)_2H$ from $Zn(CH_3)_2$, the methyl symmetric deformation band shifts from 1153 cm^{-1} for $(CH_3)_2Zn$ to 1118 cm^{-1} for $LiZn(CH_3)_2H$. Since, for a given metal, a decrease in this frequency indicates less

covalent bonding between the methyl group and the metal,[10] one can say

(10) M. Tsutsui, "Characterization of Organometallic Compounds," Part I, p. 75, Interscience Publishers, 1969.

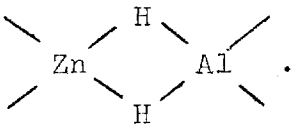
that the Zn-CH_3 bond in $LiZn(CH_3)_2H$ is more ionic than the Zn-CH_3 bond in dimethylzinc. On formation of the "ate" complex from dimethylzinc, the methyl rocking frequency also decreased. The broad Zn-H stretching mode shifted from 1450 to 1400 cm^{-1} on formation of $LiZn(CH_3)_2AlH_4$ from $LiZn(CH_3)_2H$. The Zn-CH_3 stretching mode increased in frequency on going from dimethylzinc to $LiZn(CH_3)_2H$ to $LiZn(CH_3)_2AlH_4$.

The reaction of $LiZn_2(CH_3)_4H$ with AlH_3 turns out to be just as interesting as the reaction of $LiZn(CH_3)_2H$ with AlH_3. Addition of AlH_3 to $LiZn_2(CH_3)_4H$ in THF yielded a clear solution and no precipitate. Again, this behavior indicates either the formation of a stable complex or no reaction between the species. The infrared spectrum of the reaction mixture, shown in Figure 2, contained no peak in the terminal Al-H stretching region, only a broad peak centered at 1400 cm^{-1}. Also there was no terminal Al-H deformation band in its characteristic region, 800-700 cm^{-1}; but there was a Zn-CH_3 stretching band at 700 cm^{-1}. The absence of a terminal Al-H stretching band cannot be explained by the formation of $Al(CH_3)_3$ or $LiAl(CH_3)_4$, since the Zn-CH_3 band was observed in the infrared and also no precipitate formed. The only way these results can be explained is to assume the formation of a stable complex between $LiZn_2(CH_3)_4H$ and AlH_3. The proposed structure of this complex is shown below. In view of the fact that there are no terminal aluminum hydrogen



$(LiZn_2(CH_3)_4AlH_4)$

bands in the infrared, this is the only reasonable structure that can be drawn for $LiZn_2(CH_3)_4AlH_4$. The broad band centered at 1400 cm^{-1} is in the right region for a Zn-H stretching band and a bridging Al-H stretching band. Therefore, this band is assigned to the metal hydride stretching modes for

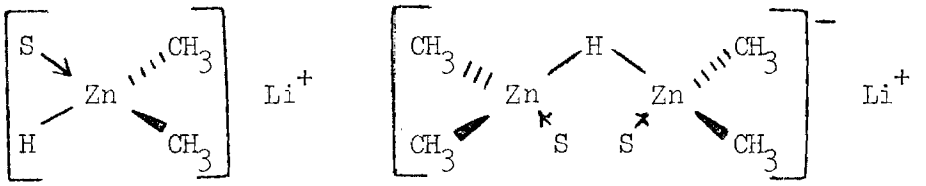


The band at 1400 cm^{-1} assigned to Zn-H stretching modes is the same as the metal hydride stretching band in $LiZn_2(CH_3)_4AlH_4$. Thus, the tentative structure written earlier for $LiZn(CH_3)_2AlH_4$ is consistent with that written for $LiZn_2(CH_3)_4AlH_4$. Referring to Table I it is interesting to notice certain trends and differences among the compounds involved in these reactions. On going from $(CH_3)_2Zn$ to $LiZn_2(CH_3)_4H$ to $LiZn_2(CH_3)_4AlH_4$ the Zn-CH_3 stretching frequency goes from 674 to 668 to a rather high value of 700 cm^{-1}. Looking at the methyl deformation frequencies, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, and $LiZn(CH_3)_2AlH_4$ appear to have about the same ionic character in the Zn-CH_3 bond, while $LiZn_2(CH_3)_4AlH_4$ appears to have more covalent character in the Zn-CH_3 bond. The Zn-H stretching frequency for $LiZn_2(CH_3)_4H$ is lower than that for $LiZn(CH_3)_2H$. These data are consistant with the structures Shriver and coworkers[11] have suggested for $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$, since one

(11) G. J. Kubas and D. F. Shirver, J. Amer. Chem. Soc., 92, 1949 (1970).

would expect the bridging Zn-H-Zn band in $LiZn_2(CH_3)_4H$ to have a lower stretching frequency than the non-bridging Zn-H band in $LiZn(CH_3)_2H$. A terminal zinc-hydride stretching vibration should occur somewhere in the range of 1600-2100 cm^{-1}.[12] The Zn-H band in $LiZn(CH_3)_2H$ is a terminal one,

(12 N. A. Bell and G. E. Coates, J. Chem. Soc., A, 823 (1968). These authors observe an 1825 cm^{-1} Zn-H absorption for $[HZnN(CH_3)C_2H_4N(CH_3)_2]$.



but solvent coordination to zinc in the complex probably causes the shift of the Zn-H stretching mode to a frequency lower than 1600 cm^{-1}.

$LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are also formed by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in 1:1 and 1:2 molar ratios. The infrared spectra of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ formed in this way, which are shown in Figures 3 and 4, are exactly the same as the spectra recorded when $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ were allowed to react with AlH_3. It makes no difference whether $LiAlH_4$ is added to $(CH_3)_2Zn$ or $(CH_3)_2Zn$ is added to $LiAlH_4$, the spectra observed when the ratio of Zn:Al is 1:1 or 2:1 are the same. As $LiAlH_4$ is added to $(CH_3)_2Zn$ there is a smooth conversion, as

shown in Scheme I, from $LiZn_2(CH_3)_2AlH_4$ to $LiZn(CH_3)_2AlH_4$. On the other hand,

$$LiAlH_4 + 2\ (CH_3)_2Zn \rightleftharpoons LiZn_2(CH_3)_4AlH_4$$

$$LiAlH_4 + LiZn_2(CH_3)_4AlH_4 \rightleftharpoons 2\ LiZn(CH_3)_2AlH_4$$

Scheme I

when $(CH_3)_2Zn$ is added to $LiAlH_4$ there is a smooth converation, as shown in Scheme II, from $LiZn(CH_3)_2AlH_4$ to $LiZn_2(CH_3)_4AlH_4$. Thus, $LiZn_2(CH_3)_4AlH_4$

$$(CH_3)_2Zn + LiAlH_4 \rightleftharpoons LiZn(CH_3)_2AlH_4$$

$$(CH_3)_2Zn + LiZn(CH_3)_2AlH_4 \rightleftharpoons LiZn_2(CH_3)_4AlH_4$$

Scheme II

can be converted to $LiZn(CH_3)_2AlH_4$ by the addition of $LiAlH_4$; and $LiZn(CH_3)_2AlH_4$ can be converted to $LiZn_2(CH_3)_4AlH_4$ by the addition of $(CH_3)_2Zn$. This means that there is a mobile equilibrium existing between $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$.

It has been known for quite some time that the reaction of a dialkylzinc with $LiAlH_4$ in diethyl ether produces ZnH_2;[5] however, no one has attempted to find out what intermediate or intermediates are involved in the alkyl-hydrogen exchange reaction. With the discovery of $LiZn(CH_3)_2AlH_4$ we believe that we have isolated the intermediate involved in this exchange reaction. The fact that $LiZn(CH_3)_2AlH_4$ is formed by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in THF is even stronger evidence. It does seem strange, though, that if this is the intermediate, why should it lead to ZnH_2 in diethyl ether and not in THF? The solutions of $LiZn(CH_3)_2AlH_4$ in THF that were being studied initially were about 0.3 to 0.4 M. They

remained clear for a few hours at room temperature then began to deposit a black solid. It was found that even after sitting one week not all of the zinc deposited from these solutions. Analysis of the black solid revealed that it contained Li:Zn:H in a molar ratio of 1.04:2.00:3.28. An X-ray powder diffraction pattern of the solid contained lines due to $LiZnH_3$ and Zn metal only. This data indicates that $LiZn_2H_5$ may precipitate from a solution of $LiZn(CH_3)_2AlH_4$, then decompose rapidly to $LiZnH_3$ and ZnH_2. On the other hand, if a 0.3 M solution of $LiZn(CH_3)_2AlH_4$ is diluted 10 fold or greater with THF, a white precipitate of ZnH_2 begins to form within five minutes. Also if $LiAlH_4$ is added to a dilute solution of $(CH_3)_2Zn$ in THF, i.e., about 0.01 M, a white precipitate of ZnH_2 begins to form within five minutes. The yields of ZnH_2, however, are low, never being greater than 50%. Reasons for the formation of ZnH_2 from $LiZn(CH_3)_2AlH_4$ in THF at a low concentration and the possible formation of $LiZn_2H_5$ at a higher concentration will be given later, after discussion of the reaction between $NaZn(CH_3)_2H$ and AlH_3. The fact that ZnH_2 is formed by way of $LiZn(CH_3)_2AlH_4$ in THF is good evidence that a compound of this structure is the intermediate involved in alkyl-hydrogen exchange involving $LiAlH_4$ and $(CH_3)_2Zn$.

The mechanism for the formation of $LiZn(CH_3)_2AlH_4$ from $LiZn(CH_3)_2H$ and AlH_3 can be visualized as occuring in the manner shown in Scheme III. Alane, which is known to be five coordinate in THF,[13] and $LiZn(CH_3)_2H$

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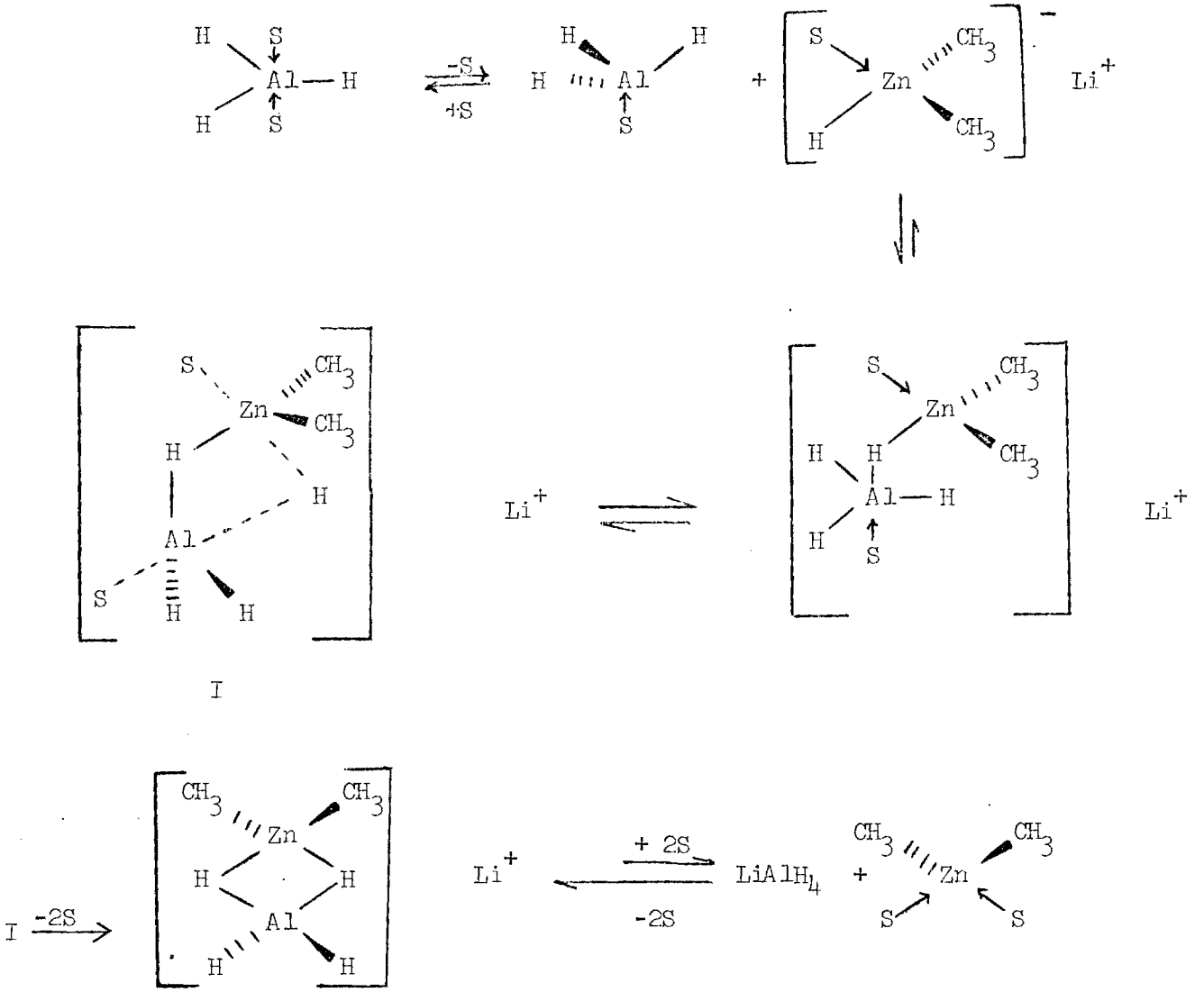
(13) R. Dautel and W. Zeil, Zeit. Elektrochem., 62, 1139 (1958).

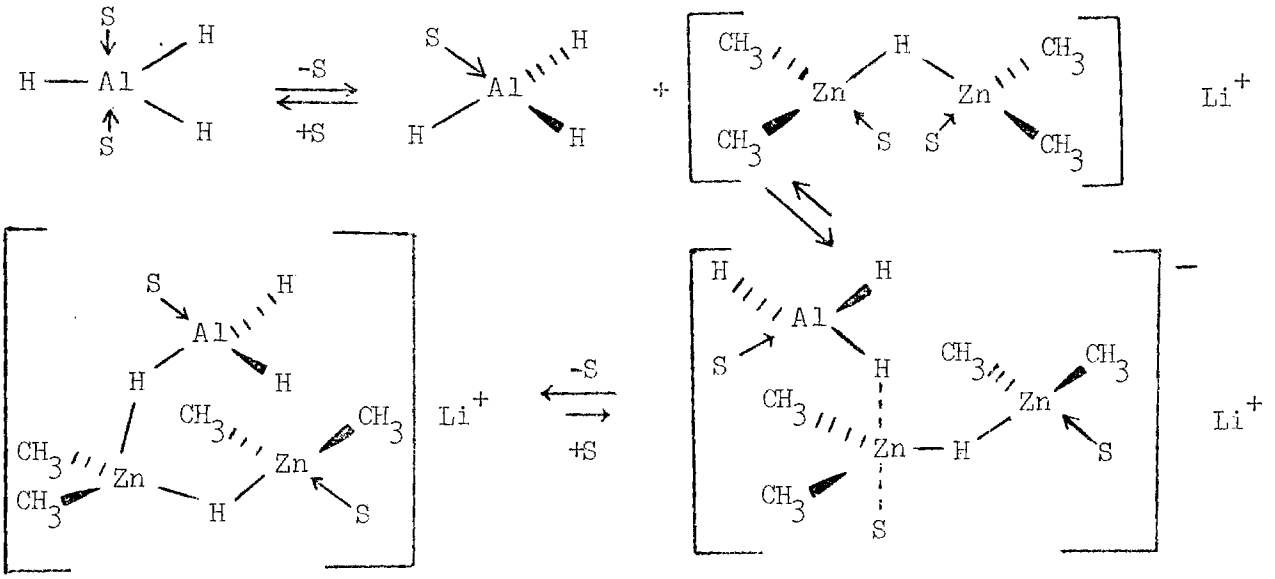


Scheme III

associate and form $LiZn(CH_3)_2AlH_4$ via intermediate I with the formation of 3-center Al-H-Zn bridge bonds with the loss of three cordinated solvent molecules. In a similar way $LiAlH_4$ and $(CH_3)_2Zn$ can associate and form $LiZn(CH_3)_2AlH_4$ with the loss of the two solvent molecules coordinated to zinc. All the steps shown in the above mechanism are suggested to be reversible; however, the equilibrium from either side lies predominantly toward $LiZn(CH_3)_2AlH_4$ since it is the only species observed in the infrared

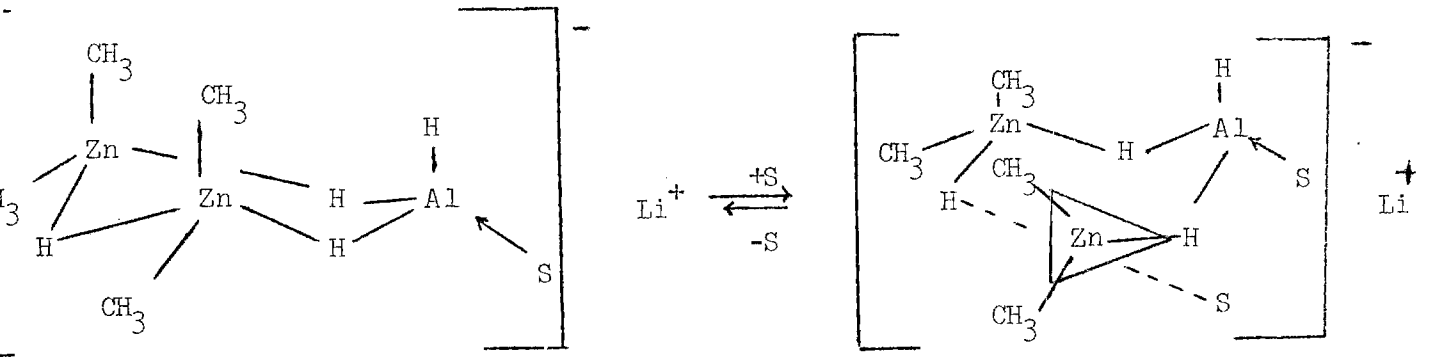
spectrum when either AlH_3 and $LiZn(CH_3)_2H$ or $LiAlH_4$ and $(CH_3)_2Zn$ are allowed to react.

The mechanism for the formation of $LiZn_2(CH_3)_4AlH_4$ from AlH_3 and $LiZn_2(CH_3)_4H$ can be visualized as occuring in the manner shown in Scheme IV. Alane and $LiZn_2(CH_3)_4H$ associate to give III by way of II and the loss of two coordinated solvent molecules. The aluminum, which is still five coordinate at this point, loses a coordinated solvent molecule to give IV. The Zn-H-Zn bridge bond is broken by a Sn_2 attack on one of the tetrahedral zinc atoms by a solvent molecule to give VI by way of intermediate V. The aluminum part of the complex is now rotated so that the non-bridging hydrogen on the aluminum will be in position to displace the solvent coordinated to the zinc atom and form an Al-H-Zn bridge bond. This process occurs by way of intermediate VII to give VIII. The final non-bridging hydrogen, which is located on the other zinc atom, now displaces the solvent molecule coordinated to the aluminum to form $LiZn_2(CH_3)_4AlH_4$ by way of intermediate IX. It is easy to see how $LiZn_2(CH_3)_4AlH_4$ could be decomposed by four solvent molecules to give $LiAlH_4$ and two $(CH_3)_2Zn$ molecules or vice versa. Again, the equilibrium from either direction lies largely in favor of $LiZn_2(CH_3)_4AlH_4$ since it is the only species observed in the infrared spectrum obtained on either reaction mixture. The critical step in this mechanism is the attack of a solvent molecule on IV to give VI. If the Zn-H-Zn bridge bond is strong enought that it cannot be broken by solvent attack on zinc, then only a compound such as IV will be formed and it will not be able to react further to give a compound with the same structure as $LiZn_2(CH_3)_4AlH_4$. We will see later that this is the case when AlH_3 reacts with $KZn_2(CH_3)_4H$.



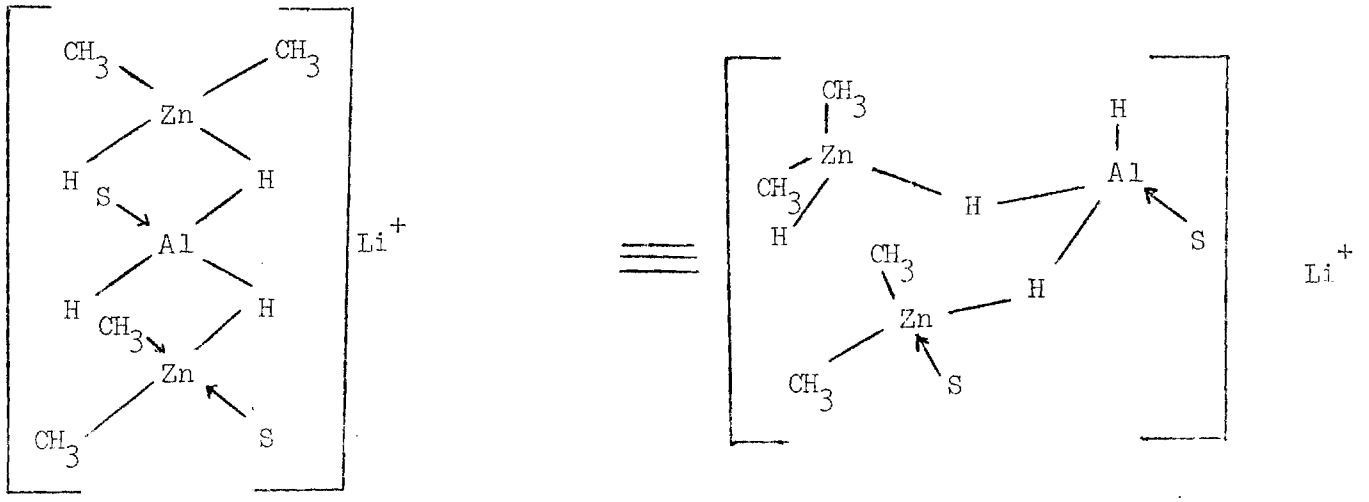
III

II

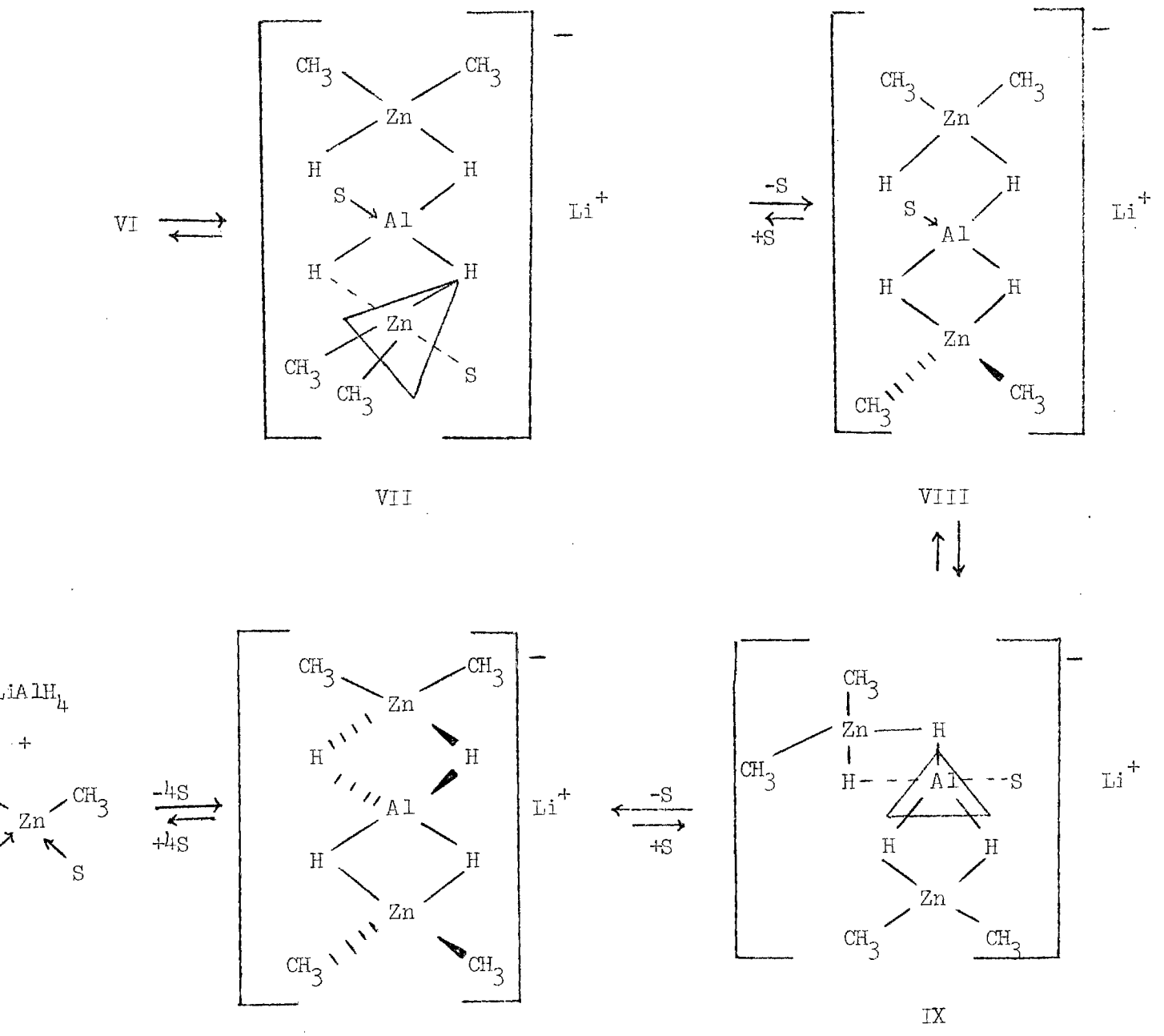


IV

V

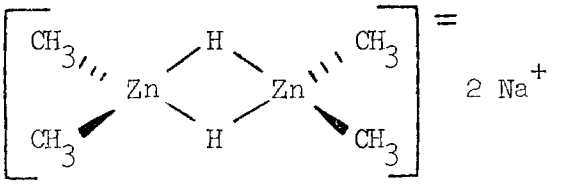


VI



Scheme IV

Now, knowing something about the structure of $LiZn(CH_3)_2AlH_4$ in solution and how it is formed, we can rationalize the behavior of $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ toward alane.[3] However, some consideration of the structures of $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF needs to be taken first. Whereas $LiZn(CH_3)_2H$ is a monomer in THF, $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ are not. $NaZn(CH_3)_2H$ is believed to be a dimer based on its infrared spectrum, shown in Figure 5. The Zn-H stretching modes appear as a broad band extending from 1000 to 650 cm^{-1} with a sharp peak superimposed at 770 cm^{-1}. The $Zn-CH_3$ stretching vibration appears at 610 cm^{-1}. In view of this unusually low Zn-H stretching frequency, we believe that in the concentration range used in these experiments $NaZn(CH_3)_2H$ exists as a dimer with a double hydrogen bridge. The proposed structure of this dimer is shown below. Both zinc atoms are believed to be



tetrahedrally coordinated. Shriver and coworkers[11] reported that $NaZn(CH_3)_2H$ is monomeric in THF; however, they did not report the concentration range over which their data apply. We feel that their solutions were not as concentrated as the ones used in this work, which were from 0.8 to 1.0 M in zinc. Shriver and coworkers[14] have also

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(14) G. J. Kubas and D. F. Shirver, Inorg. Chem., 9, 1951 (1970).

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reported that the complex $NaZn(C_6F_5)_2H$ exists as a dimer with double hydrogen bridges in diethyl ether. They report that the asymmetric Zn-H

stretching vibration for the dimer appears as a strong broad band between 1300 and 1700 cm^{-1}. However, their spectra were recorded as nujol mulls of the completely desolvated solid and not as solutions in diethyl ether. One would expect the asymmetric Zn-H stretching vibration for a double hydrogen bridged dimer to be lower than the corresponding frequency for $NaZn_2(CH_3)_4H$ which has only the Zn-H-Zn bridge bond. Inspection of Figure 6 shows that the asymmetric Zn-H stretching vibration for $NaZn_2(CH_3)_4H$ appears as a broad band between 1400 and 1150 cm^{-1} with the peak maximum occurring at 1260 cm^{-1}. Thus, it is not unreasonable that a 1.0 M solution of $NaZn(CH_3)_2H$ in THF exists as a dimer with double hydrogen bridge bonds and its asymmetric Zn-H stretching vibration occurs as low as 1000 to 650 cm^{-1}. The infrared spectrum of an approximately 1.0 M solution of $KZn(CH_3)_2H$ in THF is shown in Figure 10. It exactly matches the spectrum observed for $NaZn(CH_3)_2H$ in THF. Therefore, $KZn(CH_3)_2H$ is a dimer in THF with a structure similar to that suggested for the $NaZn(CH_3)_2H$ dimer.

When a 0.9 M solution of $NaZn(CH_3)_2H$ in THF was allowed to react with an equimolar quantity of AlH_3, an off white precipitate which was $NaZn_2H_5$ appeared immediately. After two hours all the zinc had disappeared from solution, marking complete conversion to $NaZn_2H_5$. The THF solubile product, $NaAl_2(CH_3)_4H_3$, remained in solution. The stoichiometry of the reaction is given by equation 1. The reaction of $NaAlH_4$ with $(CH_3)_2Zn$ in a 1:1

$$[NaZn(CH_3)_2H]_2 + 2\ AlH_3 \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \qquad (1)$$

molar ratio also yielded $NaZn_2H_5$ and $NaAl_2(CH_3)_4H_3$, see equation 2.

$$2\ NaAlH_4 + 2\ (CH_3)_2Zn \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \qquad (2)$$

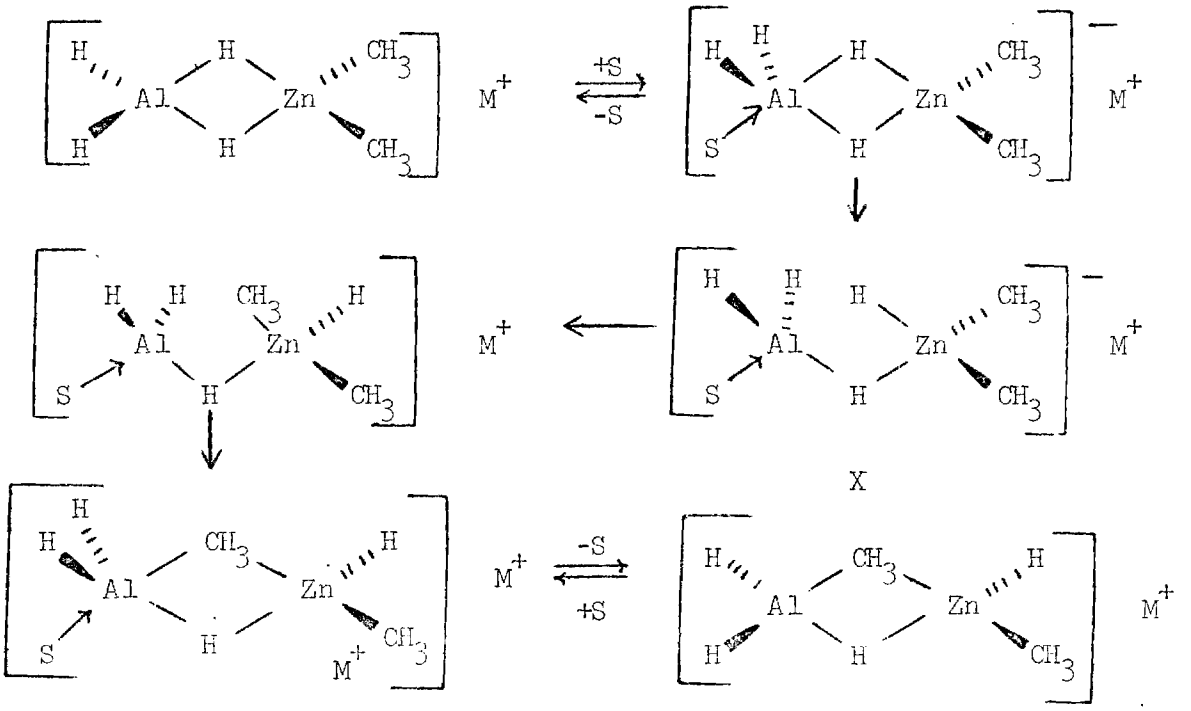
In this case, however, a precipitate did not appear until a few minutes after the reactants had been mixed and in addition all the zinc disappeared from solution only after a period of one week. The reaction of $NaAl(CH_3)_2H_2$ with ZnH_2 in a 1:1 molar ratio also yielded $NaZn_2H_5$ and $NaAl_2(CH_3)_4H_3$ (see equation 3). In this case, a clear solution remained

$$2\ NaAl(CH_3)_2H_2 + 2\ ZnH_2 \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \qquad (3)$$

for about twenty minutes before any solid began to form. After sitting for a period of one week all the zinc finally disappeared from the solution. In each of these three cases the intermediate leading to the products could be observed by infrared spectroscopy. Figure 8 contains infrared spectra of the supernatent solution from the reaction of $NaAlH_4$ with $(CH_3)_2Zn$ in a 1:1 molar ratio after 5 minutes, 2 1/2 hours, 28 hours, 4 days and 7 days. Only after 7 days does the spectrum approach that of $NaAl_2(CH_3)_4H_3$. The remainder of the spectra which are of the intermediate leading to the product, are essentially identical; therefore, the spectrum of the reaction mixture after 5 minutes is representative and will be looked at in detail. There is a very broad band in the metal-hydrogen stretching region extending from 1800 to 1200 cm^{-1}. This band has a maximum absorption at 1615 and 1400 cm^{-1} with a trough in between. In the 800-600 cm^{-1} region the metal-hydrogen deformation (760 cm^{-1}) and the metal-carbon stretching vibration (670 cm^{-1}) occur. This spectrum is very similar to the spectrum observed for $LiZn(CH_3)_2AlH_4$ except that in this case the terminal Al-H asymmetric stretching vibration occurs at 1615 cm^{-1}. In view of this very close correspondance, the intermediate is probably $NaZn(CH_3)_2AlH_4$. The intermediate involved in the formation of $NaZn_2H_5$ from $NaAl(CH_3)_2H_2$ and ZnH_2 must also be $NaZn(CH_3)_2AlH_4$, since an infrared spectrum of the clear solution initially formed contained these

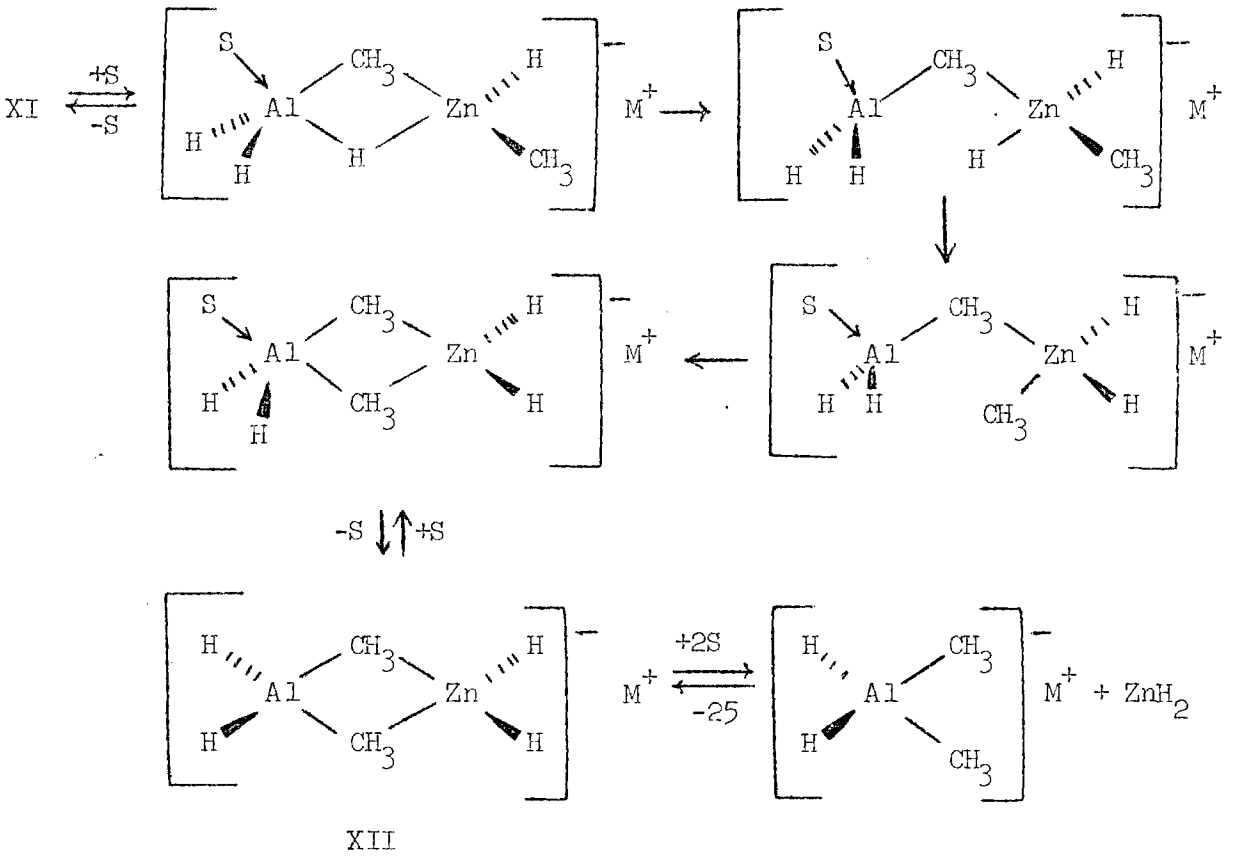
same bands. Figure 5 contains infrared spectra of the supernatent solution from the reaction of $NaZn(CH_3)_2H$ with AlH_3 after 5 minutes and 25 hours. The spectrum of the supernatent left after 5 minutes contained a broad band extending from ~1550 to 1200 cm^{-1} with no well defined maximum. The rest of the spectrum corresponds to $NaAl_2(CH_3)_4H_3$ which was also formed. The broad band extending from 1550 to 1200 cm^{-1} could be due to $NaZn(CH_3)_2AlH_4$; however, it seems unlikely that the same intermediate should be involved in this reaction as in the above two since the rates of formation of $NaZn_2H_5$ are so different. If $NaZn(CH_3)_2AlH_4$ were the actual intermediate leading to $NaZnH_5$ from the reaction of $NaZn(CH_3)_2H$ with AlH_3, one would expect it to take about a week for all the zinc to disappear from solution, but instead it takes only a few hours. The only reasonable explanation is that the latter reaction proceeds by way of a different mechanism than the first two - a mechanism that involves different intermediates. It was mentioned earlier that $LiZn(CH_3)_2AlH_4$ formed from the reaction of either $LiZn(CH_3)_2H$ with AlH_3 or $LiAlH_4$ with $(CH_3)_2Zn$ begins to decompose slowly after a few hours, but that even after a week not all the zinc was deposited from the solution. Also it was noted that when either of these reactions were carried out in dilute solution ZnH_2 precipitated. This same phenomenon occurs when either $NaAlH_4$ and $(CH_3)_2Zn$ or $NaZn(CH_3)_2H$ and AlH_3 are allowed to react in dilute solution. When alane was added to a dilute solution of $NaZn(CH_3)_2H$ in THF (less than 0.01 M), a clear solution persisted for about three hours, then a white precipitate began to form. The white precipitate was found to be ZnH_2. It took about 8 days for all the zinc to be deposited from solution. Earlier it was mentioned that $NaZn(CH_3)_2H$ is dimeric in solution above 0.2 M and monomeric in dilute solution.

$LiZn(CH_3)_2H$ was found to be monomeric over all concentrations employed in this work. From these observations it appears that monomeric $MZn(CH_3)_2H$ compounds react with alane to give $MZn(CH_3)_2AlH_4$ which yields MZn_2H_5 in solutions above 0.2 M and ZnH_2 in more dilute solutions. Reactions of $MAlH_4$ compounds with $(CH_3)_2Zn$ proceed similarily. Since the only difference in these reaction is the concentration of the intermediate leading to products ($MZn(CH_3)_2AlH_4$), the different concentration of the intermediate must be the reason why different products are observed. The rate of inter-molecular exchange appears to be greater than intramolecular exchange and at higher concentrations intermolecular exchange is the major reaction pathway leading to MZn_2H_5. At lower concentrations the rate of inter-molecular exchange is slowed down enough that intramolecular exchange becomes the predominant pathway and the major product becomes ZnH_2. The mechanism for the intramolecular pathway can be represented by the steps shown in Scheme V.



X

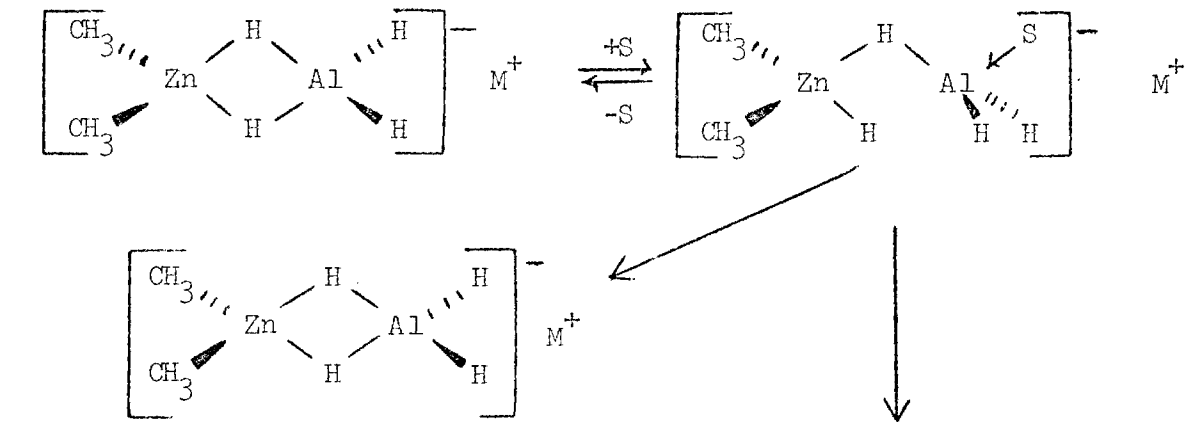
XI

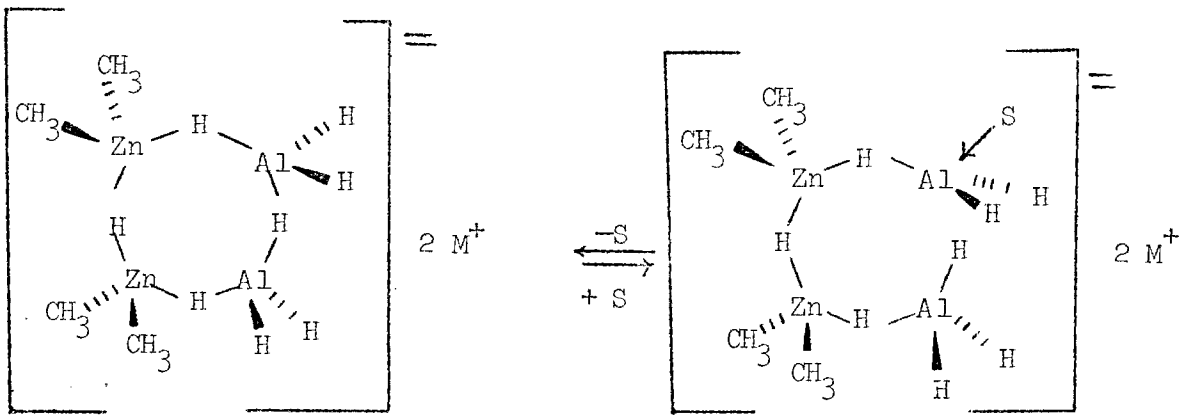


XII

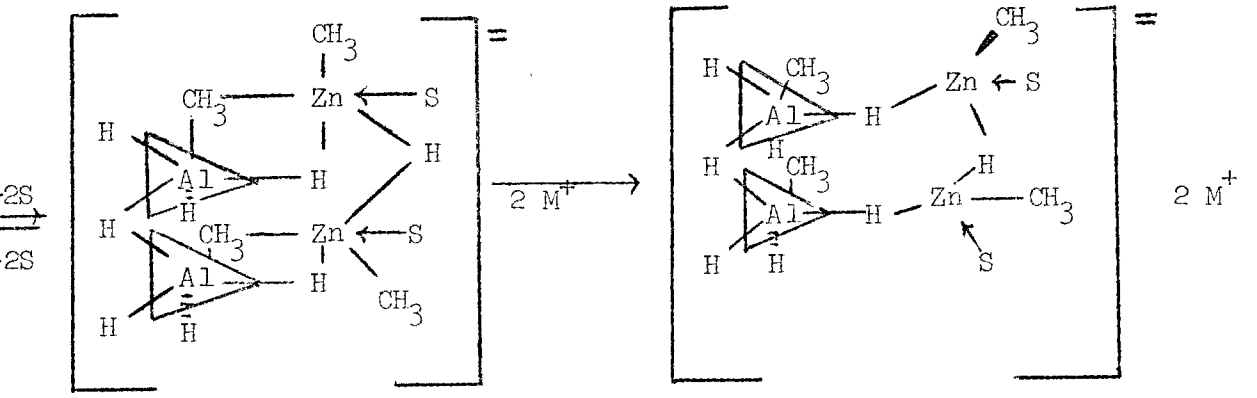
Scheme V

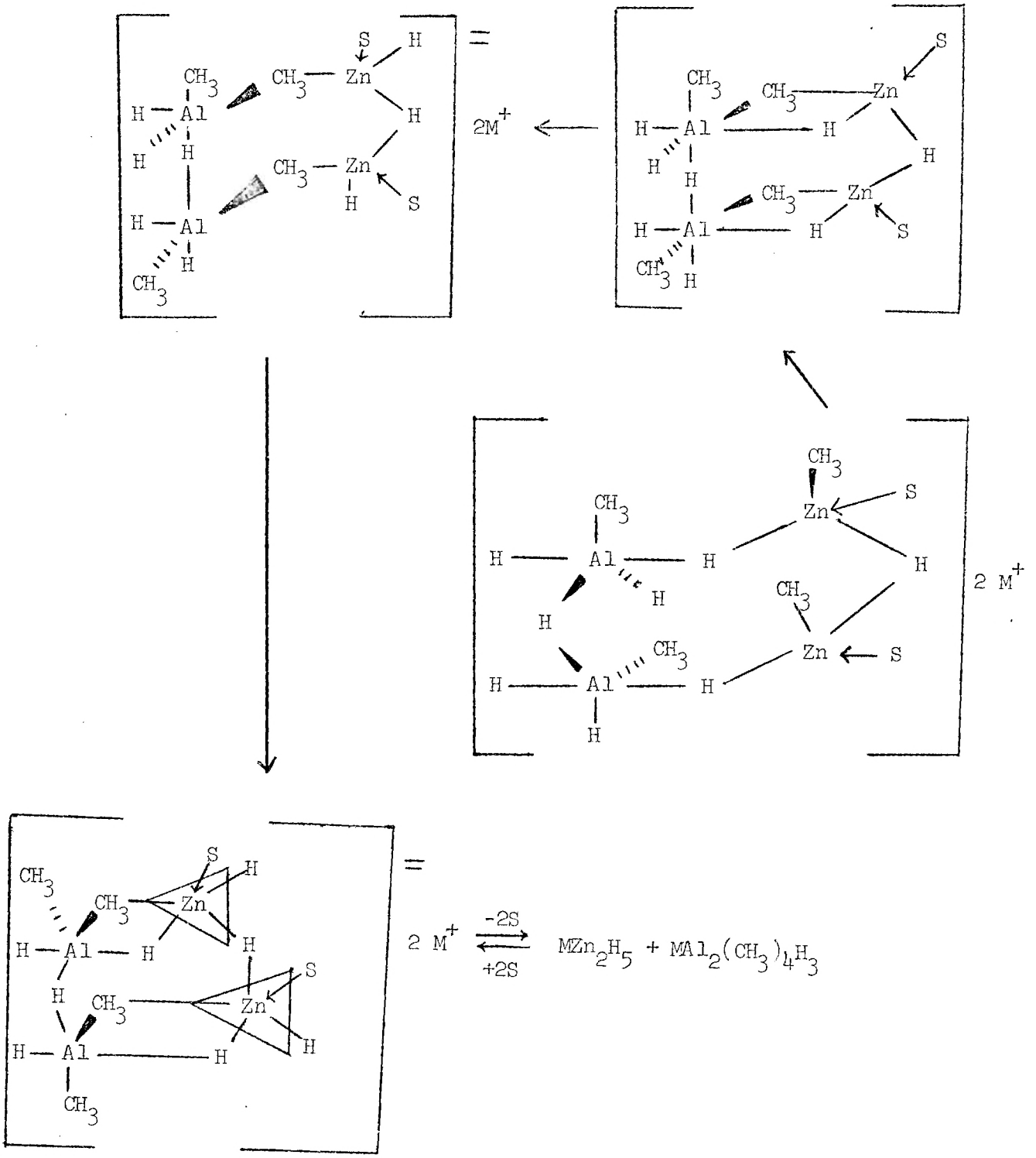
The mechanism for the intermolecular pathway can be represented by the steps shown in Scheme VI. Consideration of these two detailed mechanisms are initiated by solvent cleavage of the double hydride bridge bond between aluminum and zinc in $MZn(CH_3)_2AlH_4$ to give intermediate X. Now, as shown in Scheme V, if the concentration of $MZn(CH_3)_2AlH_4$ is low enough, X will not react with another molecule of $MZn(CH_3)_2AlH_4$, but will undergo rotation about the remaining hydrido-aluminum-zinc bridge bond placing one of the zinc's methyl groups in position to form a bridge bond between zinc and aluminum, as in XI. XI then undergoes a similar exchange to give XII, which yields ZnH_2. It must be emphasized that all the steps leading





XIII

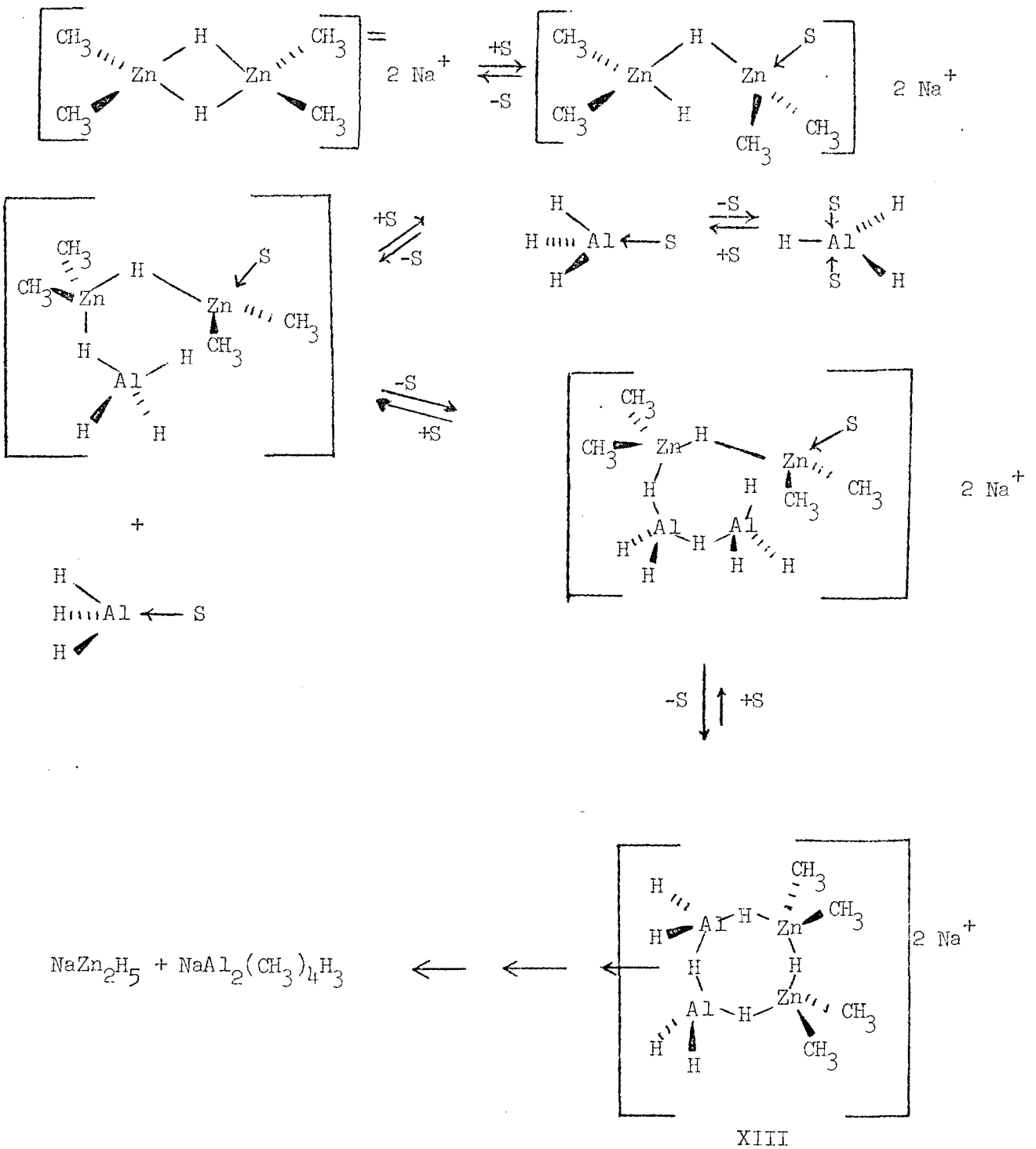




Scheme VI

from X to XII are reversible. The only reason ZnH_2 is formed at all is because the rate of reaction of X with $MZn(CH_3)_2AlH_4$ is slowed down enough at low concentration that the overall rate of conversion from X to ZnH_2 and $MAl(CH_3)_2H_2$ increases. Evidence for this position is the fact that at 0.3 M ZnH_2 reacts with $NaAl(CH_3)_2H_2$ to form $NaZn_2H_5$ and $NaAl_2(CH_3)_4H_3$. The equilibria involving all these species are so mobile that one could probably react MZn_2H_5 with $MAl_2(CH_3)_4H_3$ in a very dilute solution and get ZnH_2 (although this has not been shown experimentally).

We are now ready to offer a detailed mechanism for the conversion of $NaZn(CH_3)_2H$ to $NaZn_2H_5$ by reaction with alane in solutions above 0.1 M concentration. As was pointed out earlier the rate at which this reaction yields insoluble products is much greater than the rate at which $LiZn(CH_3)_2H$ reacts with alane to yield insoluble products at the same concentration. We pointed out earlier that this rate increase is due to a difference in reaction pathway. $LiZn(CH_3)_2H$ reacts with alane to give $LiZn(CH_3)_2AlH_4$ which disappears in the manner described in Scheme VI. $NaZn(CH_3)_2H$ does not react with alane to give $NaZn(CH_3)_2AlH_4$, as was pointed out earlier in view of the infrared spectra recorded during the reaction. This difference in behavior must be due to the fact that $NaZn(CH_3)_2H$ is a dimer at concentrations greater than 0.1 M. A detailed step by step mechanism for this reaction is given in Scheme VII. The first step in this reaction is solvent cleavage of one of the two bridging Zn-H-Zn bonds, then two molecules of alane can add rapidly to give intermediate XIII. This same intermediate was proposed in Scheme VI. XIII then follows the same path as given in Scheme VI to yield $NaZn_2H_5$. The infrared spectrum of the intermediate observed during this reaction, shown in Figure 5, is probably due to XIII. Of course, XIII could



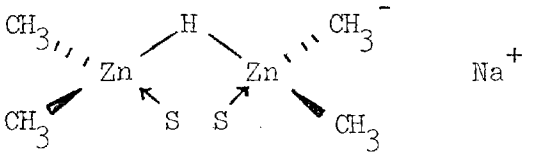
$NaZn_2H_5 + NaAl_2(CH_3)_4H_3$

XIII

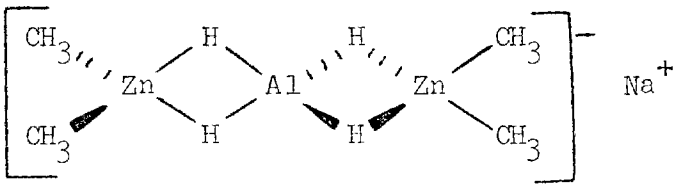
Scheme VII

decompose to give $NaZn(CH_3)_2AlH_4$ since such a mobile equilibrium is present in these systems, but evidently its rate of collapse to give $NaZn_2H_5$ is more rapid.

The reaction of $NaZn_2(CH_3)_4H$ with alane behaves similar to the reaction of $LiZn_2(CH_3)_4H$ with alane ($NaZn_2(CH_3)_4AlH_4$ is formed). The infrared spectra of $NaZn_2(CH_3)_4H$ and $NaZn_2(CH_3)_4AlH_4$ are shown in Figure 6. The asymmetric zinc-hydrogen stretching frequency for $NaZn_2(CH_3)_4H$ occurs as a broad peak with its maximum at 1260 cm^{-1}. Its zinc-carbon stretching mode occurs at 630 cm^{-1}. This spectrum is similar to that of $LiZn_2(CH_3)_4H$, so that $NaZn_2(CH_3)_4H$ should have a structure analogous to that of $LiZn_2(CH_3)_4H$. The spectrum of $NaZn_2(CH_3)_4AlH_4$ is



also very similar to that of $LiZn_2(CH_3)_4AlH_4$. There is a very broad peak in the metal-hydrogen stretching region with a small shoulder at 1480 and maximum at 1380 cm^{-1}. There is no band in the terminal Al-H stretching or deformation region. The zinc-carbon stretching vibration occurs at 680 cm^{-1}. The structure of $NaZn_2(CH_3)_4AlH_4$, therefore, must be similar to that of $LiZn_2(CH_3)_4AlH_4$. The mechanism of the formation of



($NaZn_2(CH_3)_4AlH_4$)

$NaZn_2(CH_3)_4AlH_4$ from $NaZn_2(CH_3)_4H$ and alane is the same as that given

in Scheme IV.

The reactions of $KZn(CH_3)_2H$ with alane and $KAlH_4$ with $(CH_3)_2Zn$ in 1:1 molar ratio behave differently than the corresponding sodium system, although KZn_2H_5 is formed in both reactions. The difference is due to the fact that there is no concentration dependence by the reaction product and the rate of formation of KZn_2H_5 is much faster than in the sodium system. The reaction of $KAlH_4$ with $(CH_3)_2Zn$ in 1:1 molar ratio is complete within three hours regardless of the concentration of the starting materials and the reaction of $KZn(CH_3)_2H$ with alane is complete within five minutes. In view of this large rate increase and the non-concentration dependence of the product, the mechanism for the formation of KZn_2H_5 must be different from that presented for the sodium systems. One would expect $KZn(CH_3)_2AlH_4$ to be involved in the reaction of $KAlH_4$ with $(CH_3)_2Zn$; however, infrared spectra analysis of the reaction mixture in its intermediate stages failed to show the bands characteristic of the $[Zn(CH_3)_2AlH_4]^{-1}$ system. One such spectrum is shown in Figure 9. There is a broad band extending from 1500-1150 cm^{-1} in the metal-hydrogen stretching region. This band has its maximum absorption at 1380 cm^{-1} and has a shoulder at 1300 cm^{-1}. In the 700-600 cm^{-1} region there is a band at 675 cm^{-1} which has a shoulder at 650 cm^{-1}. Attempts to record infrared spectra of the intermediates involved in the reaction of $KZn(CH_3)_2H$ with alane were unsuccessful. It may be that the mechanism of these reactions are similar to those given for the sodium system, but due to lack of evidence we cannot say definitely whether this is the truth or not.

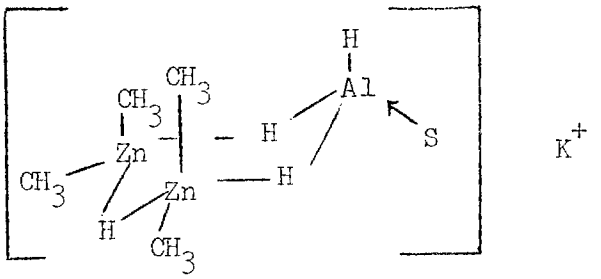
The reaction of $KZn_2(CH_3)_4H$ with alane differs considerably from the reaction of $LiZn_2(CH_3)_4H$ and $NaZn_2(CH_3)_4H$ with alane. While the

latter two reactions yield $LiZn_2(CH_3)_4AlH_4$ and $NaZn_2(CH_3)_4AlH_4$, $KZn_2(CH_3)_4H$ reacts with either one or two equilivalents of alane to yield KZn_2H_5 (see equations 4 and 5). Alane does not react with $KZn_2(CH_3)_4H$ to give

$$KZn_2(CH_3)_4H + AlH_3 \rightarrow 4/5\ KZn_2H_5 + 1/5\ KZn_2(CH_3)_5 + (CH_3)_3Al \qquad (4)$$

$$KZn_2(CH_3)_4H + 2\ AlH_3 \rightarrow KZn_2H_5 + 2\ Al(CH_3)_2H \qquad (5)$$

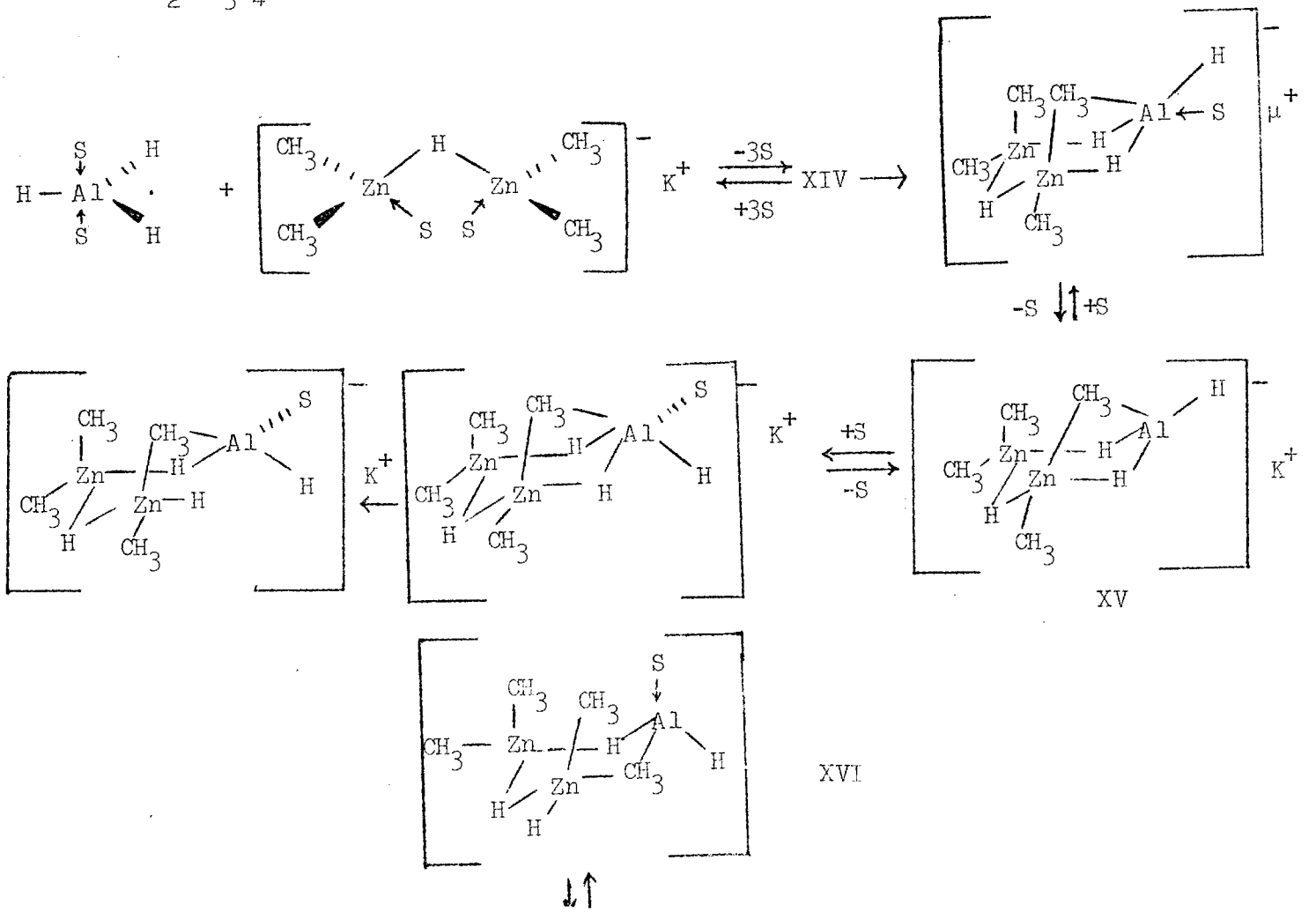
$KZn_2(CH_3)_4AlH_4$. One would have expected $KZn_2(CH_3)_4H$ to react with alane in 1:2 molar ratio to give ZnH_2 as was the case with $LiZn_2(CH_3)_4H$ and $NaZn_2(CH_3)_4H$. More evidence along this line is provided by considering infrared spectral evidence. When $KAlH_4$ and $(CH_3)_2Zn$ are allowed to react in a 1:2 molar ratio, a clear solution results. The infrared spectrum of this solution, shown in Figure 10, is exactly like the infrared spectrum of $LiZn_2(CH_3)_4AlH_4$ and $NaZn_2(CH_3)_4AlH_4$. If this clear solution is allowed to stand, after about ten minutes a white solid which is KZn_2H_5 begins to precipitate. But if immediately after the clear solution is formed an equilivant of alane is added, ZnH_2 is formed. In view of this evidence one can conclude that $KZn_2(CH_3)_4AlH_4$ is formed by the reaction of $KAlH_4$ with $(CH_3)_2Zn$ in a 1:2 molar ratio. Now when alane is added to $KZn_2(CH_3)_4H$ in a 1:1 molar ratio, a white precipitate begins to form immediately. An infrared spectrum of the supernatent left after five minutes reaction time is shown in Figure 10. This spectrum is clearly not that of $KZn_2(CH_3)_4AlH_4$, but is assigned to a compound like that of intermediate IV shown in Scheme IV (mechanism for the formation of $LiZn_2(CH_3)_4AlH_4$). This intermediate compound is labeled XIV, and is shown below. Its spectrum contains three bands in the metal-hydrogen stretching region, one at 1510, another at 1390, and the third at 1340 cm^{-1}. The band at

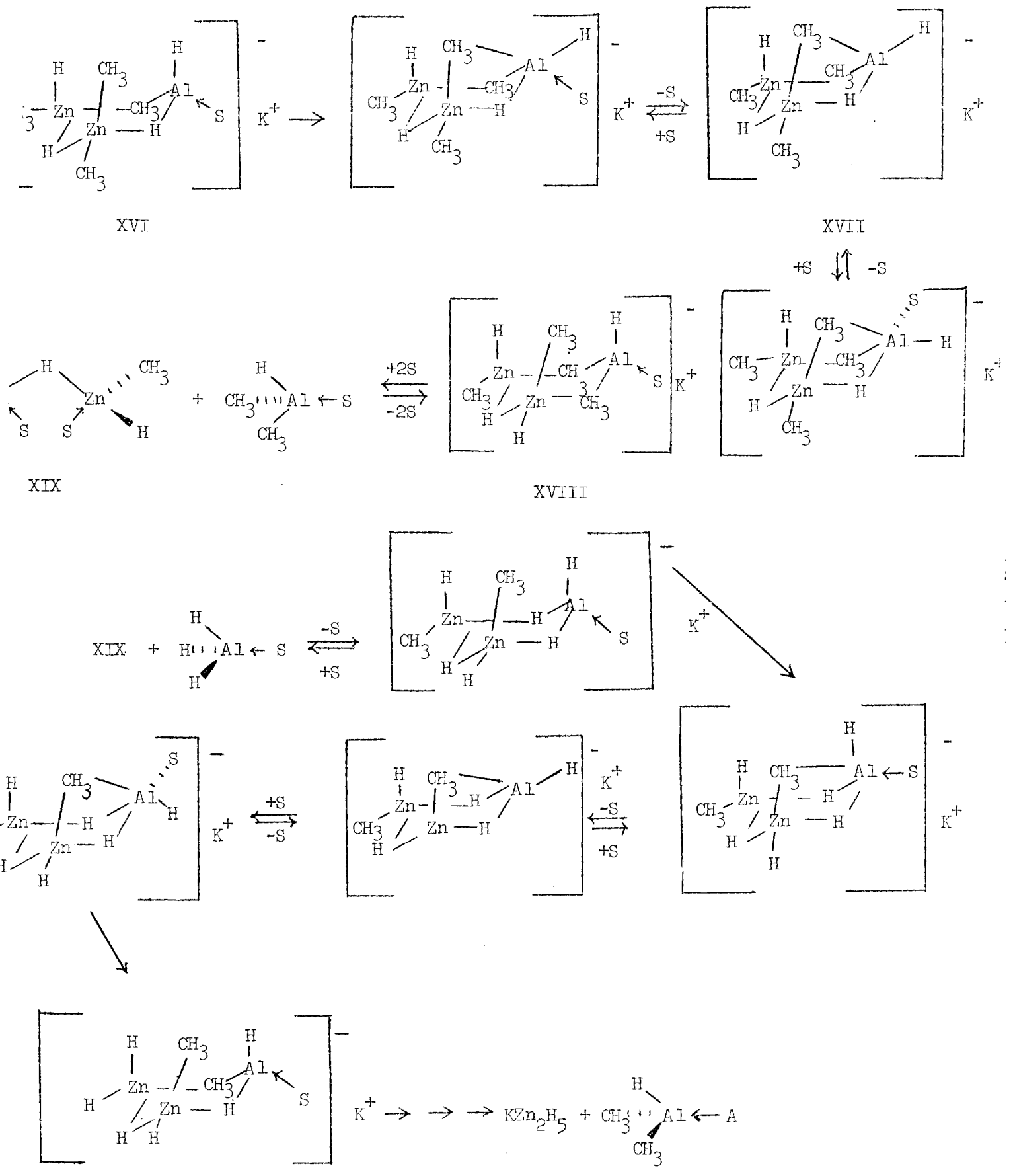


XIV

1510 cm^{-1} is assigned to the stretching modes of the terminal Al-H group in XIV. The band at 1390 cm^{-1} is assigned to the stretching modes of the bridging hydrogen between aluminum and zinc. The band at 1340 cm^{-1} is assigned to the stretching modes of the bridging hydrogen between the two zinc atoms. Two bands are observed in the 700-600 cm^{-1} region, one at 680 cm^{-1} is assigned to the terminal Al-H deformation modes, while the band at 640 cm^{-1} is assigned to the zinc carbon stretching modes. Earlier it was pointed out that the critical step in the formation of $LiZn_2(CH_3)_4AlH_4$ is the attack of a solvent molecule on intermediate IV to cleave the Zn-H-Zn bridge bond. Evidently, in the reaction of $KZn_2(CH_3)_4H$ with alane, the Zn-H-Zn bridge bond in XIV is to strong to be cleaved by a solvent molecule and $KZn_2(CH_3)_4AlH_4$ is never formed. Instead of forming $KZn_2(CH_3)_4AlH_4$, XIV undergoes intramolecular exchange to yield KZn_2H_5. In Scheme IV it was pointed out that a mobile equilibrium exists between $LiZn_2(CH_3)_4AlH_4$ and intermediate IV. When lithium or sodium is the cation, the equilibrium lies in the direction of $MZn_2(CH_3)_4AlH_4$; however, when potassium is the cation, the equilibrium lies in the direction of XIV. Thus, when $KAlH_4$ and $(CH_3)_2Zn$ are allowed to react in a 1:2 molar ratio, the initial product is $KZn_2(CH_3)_4AlH_4$; however, it is converted to XIV after a few minutes. Intermediate XIV then reacts in a way to be described shortly to give KZn_2H_5. Proof that both reactions proceed by way of the same intermediates is offered by the fact that an infrared spectrum of the supernatent solution (taken about ten minutes after KZn_2H_5 begans

to precipitate) was exactly the same as the spectrum observed after five minutes in the reaction of $KZn_2(CH_3)_4H$ with alane in a 1:1 molar ratio. This spectrum is shown in Figure 11. It is interesting to note that both the reaction of $KAlH_4$ with $(CH_3)_2Zn$ in 1:2 molar ratio and the reaction of $KZn_2(CH_3)_4H$ with alane in 1:1 molar ratio are complete within four hours. The degree of reaction is measured by the ratio of K:Zn:Al remaining in solution. In both reactions the ratio of K:Zn:Al remained constant at 1:2:5 after four hours. Infrared spectra of the supernatent solutions remaining after four hours contained no bands in the metal hydrogen stretching region. Thus, all the active hydrogen was contained in KZn_2H_5. The fact that both reactions proceed at the same rate and to the same degree of completion is even more evidence that they both proceed by the same mechanism. A detailed step by step mechanism for the reaction of $KZn_2(CH_3)_4H$ with alane is shown in Scheme VIII.





Scheme VIII

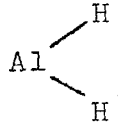
The first step involves a series of solvent displacements, like those shown in Scheme IV, to give intermediate XIV. This intermediate then undergoes an intramolecular solvent displacement to yield XV. The driving force for such a reaction would be to better delocalize the negative charge residing at the end of the ring where the two zinc atoms are located. The potassium "ate" complexes are a lot more ionic than the one's of lithium or sodium. Therefore, in the potassium "ate" complexes more negative charge must be carried by the anion. A decrease in charge delocalization is probably the major reason why the Zn-H-Zn bridge bond in XIV is not cleaved by solvent. If the bridge bond were cleaved, there would be an unfavorable build up of negative charge on one of the zinc atoms. For this reason Scheme VIII does not show any solvent initiated ring cleavages, but only intramolecular rearrangements that keep the ring intact. The next step in the mechanism is solvent displacement of the Zn-H-Al bridge bond in the double bridged part of the molecule to give XVI. This displacement keeps the Zn-CH_3-Al bridge bond and the ring intact. The driving force for this reaction is greater charge delocalization also, since it is a known fact that a methyl group releases more negative charge than a hydride group. By putting the methyl group in a bridging position its electron releasing characteristics are decreased. Intermediate XVI then undergoes the same series of reactions to give XVIII as XIV did to give XVI. Intermediate XVIII then undergoes nucleophilic attack by two solvent molecules on the two zinc atoms to yield dimethylalane and XIX. Up to this point the mechanism is the same regardless of whether $KZn_2(CH_3)_4H$ and alane are allowed to react in 1:2 or 1:1 ratio or whether the reaction was between $KAlH_4$ and $(CH_3)_2Zn$ in 1:2 ratio. If the initial ratio of

$KZn_2(CH_3)_4H$ to alane had been 1:2, then XIX reacts with another molecule of alane through the steps shown in Scheme VIII to give KZn_2H_5 and another equivalent of dimethylalane. On the other hand, if the reaction was between $KZn_2(CH_3)_4H$ and alane in a 1:1 ratio or $KAlH_4$ and $(CH_3)_2Zn$ in 1:2 ratio, XIX would be reduced by means of a complicated series of equilibrium reactions in which all the active hydrogen is removed from the solution and ends up as KZn_2H_5.

In this paper we have tried to present reasonable mechanisms, based on the information gathered in this study, for the exchange reactions between the zinc ate complexes $MZn(CH_3)_2H$, $MZn_2(CH_3)_4H$, and alane. In these mechanisms we have tried to indicate the importance of the role of the solvent in exchange reactions of this type. We have shown the dependence of the reaction between $(CH3)_2Zn$ and $NaAlH_4$ on solvent concentration. The fact that $LiZn(CH_3)_2AlH_4$ is formed by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ is very good evidence that it is the intermediate involved in the formation of ZnH_2 from these two reactants. This is the first report of any evidence concerning intermediates involved in the reaction of $MAlH_4$ compounds with Group II metal alkyls. Work is now in progress to study the mechanism of the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in diethyl ether. In a later paper we will discuss the mechanisms of the reactions of the zinc ate complexes, $MZn(CH_3)_2H$ and $MZn_2(CH_3)_4H$, with $MAlH_4$ compounds. The use of $LiZn(CH_3)_2AlH_4$ as a precussor to the trimetal hydride, $LiZnAlH_6$, will also be discussed in a later report.

Table I.

Infrared Spectra of $(CH_3)_2Zn$, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ in THF[a]

Obsd IR bands, cm^{-1}[b]					
$(CH_3)_2Zn$	$LiZn(CH_3)_2H$	$LiZn_2(CH_3)_4H$	$LiZn(CH_3)_2AlH_4$	$LiZn_2(CH_3)_4AlH_4$	Approx. Assignment
674 vs	680 vs	668 vs	690 vs	700 vs	Zn-C stretch
			720 sh,s		
			775 s		Al-H deformation
840 m	795 w				CH_3 rock
1153 m	1118 m	1120 m	1118 m	1140 m	CH_3 deformation
			1162 m	1170 w	
	1450 br[c], s	1290 br,[c] s			Zn-H stretch
			1400 br, s	1400 br, s	 Zn stretch
			1660 br, vs		terminal Al-H stretch

[a] All spectra were run with THF as reference; [b] Abbreviations: w, weak; m, medium; s, strong, sh, shoulder; br, broad; [c] These bands were very broad. The frequency given is approximately the center of the band.

Figure I. Infrared spectra of (a) $(CH_3)_2Zn$ in THF, (b) $LiZn(CH_3)_2H$ in THF and (c) $LiZn(CH_3)_2AlH_4$ in THF

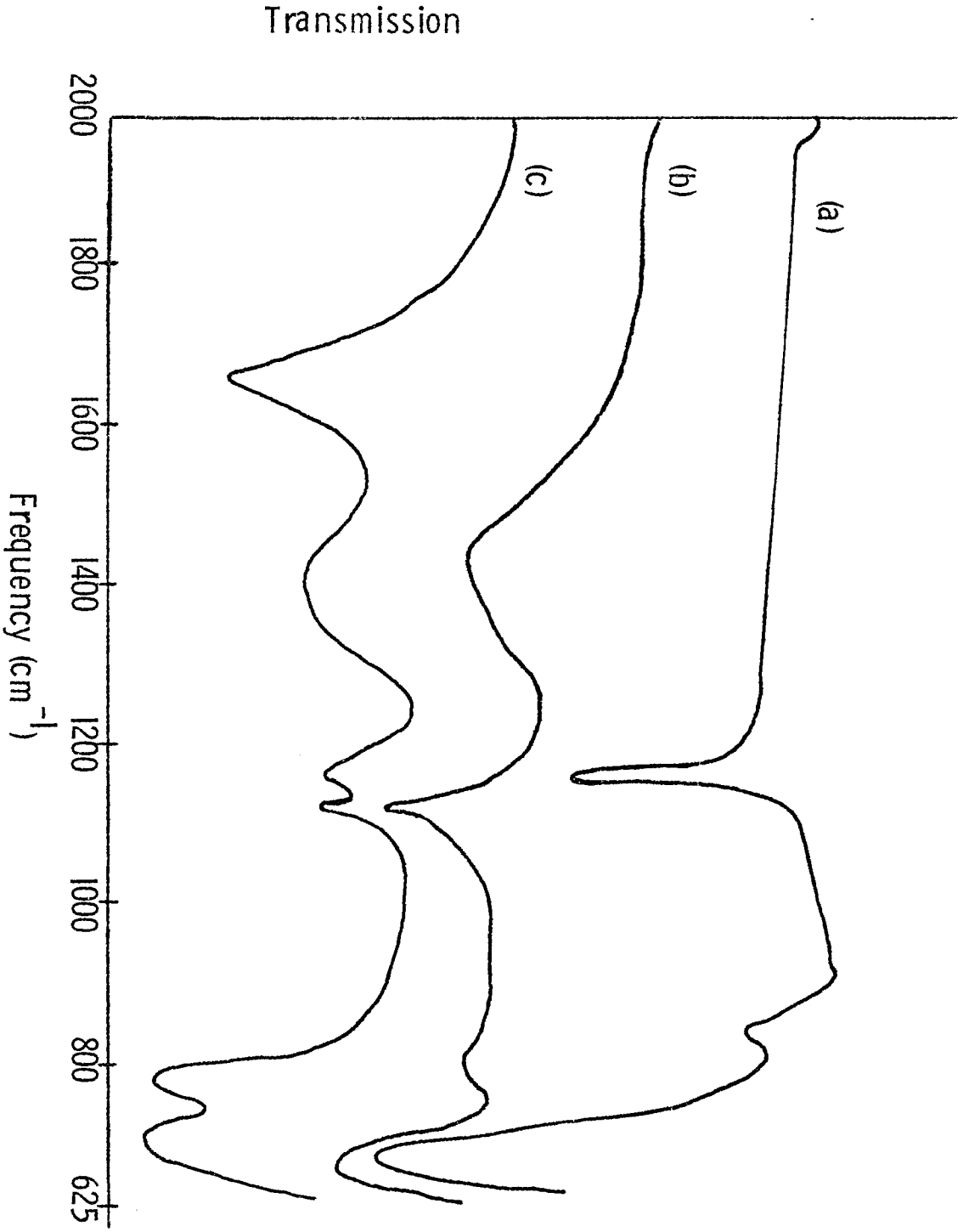

Transmission
2000
1800
1600
1400
1200
1000
800
625
Frequency (cm⁻¹)
(a)
(b)
(c)

Figure 2. Infrared spectra of (a) $(CH_3)_2Zn$ in THF, (b) $LiZn_2(CH_3)_4H$ in THF and (c) $LiZn_2(CH_3)_4AlH_4$ in THF

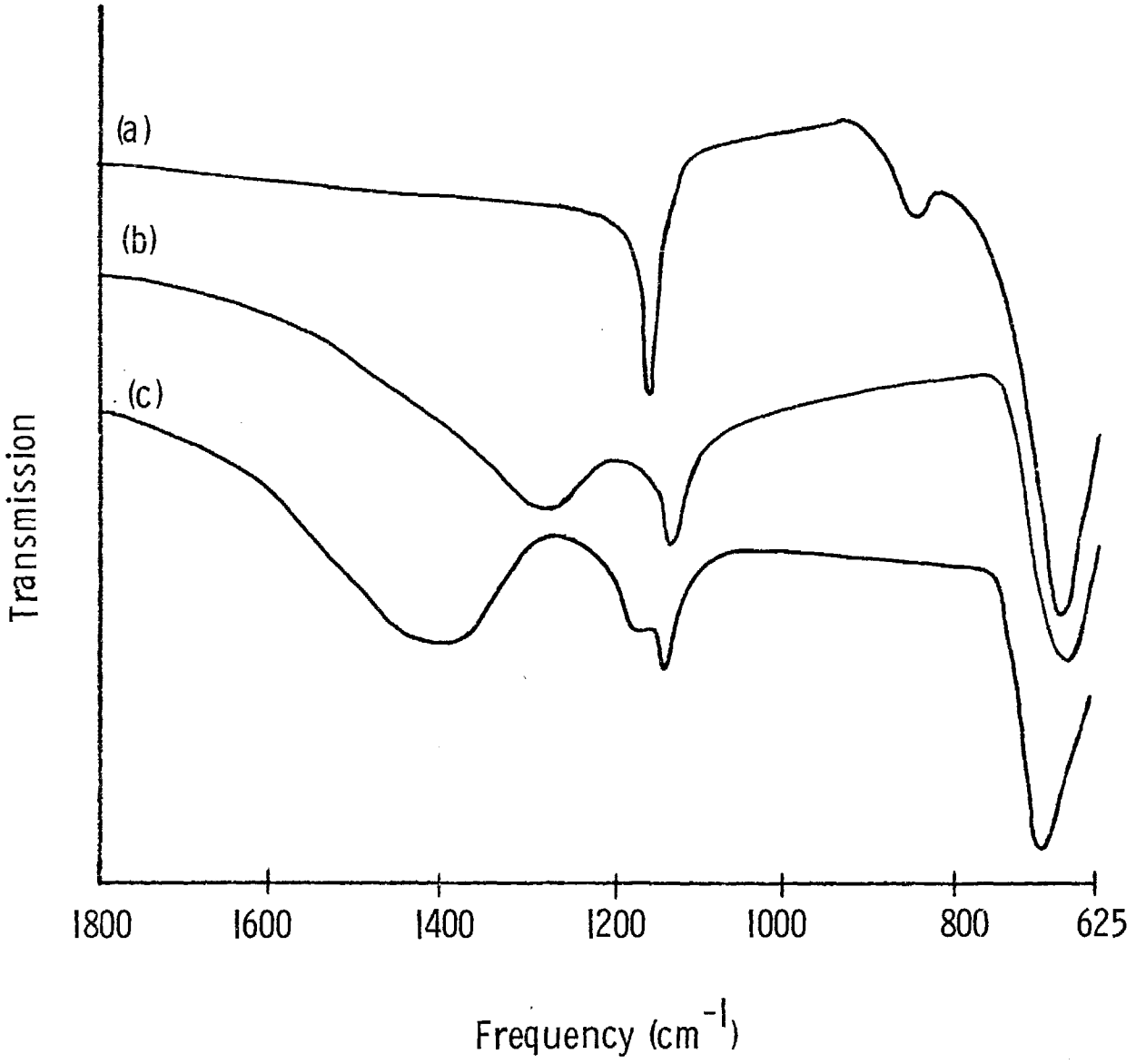
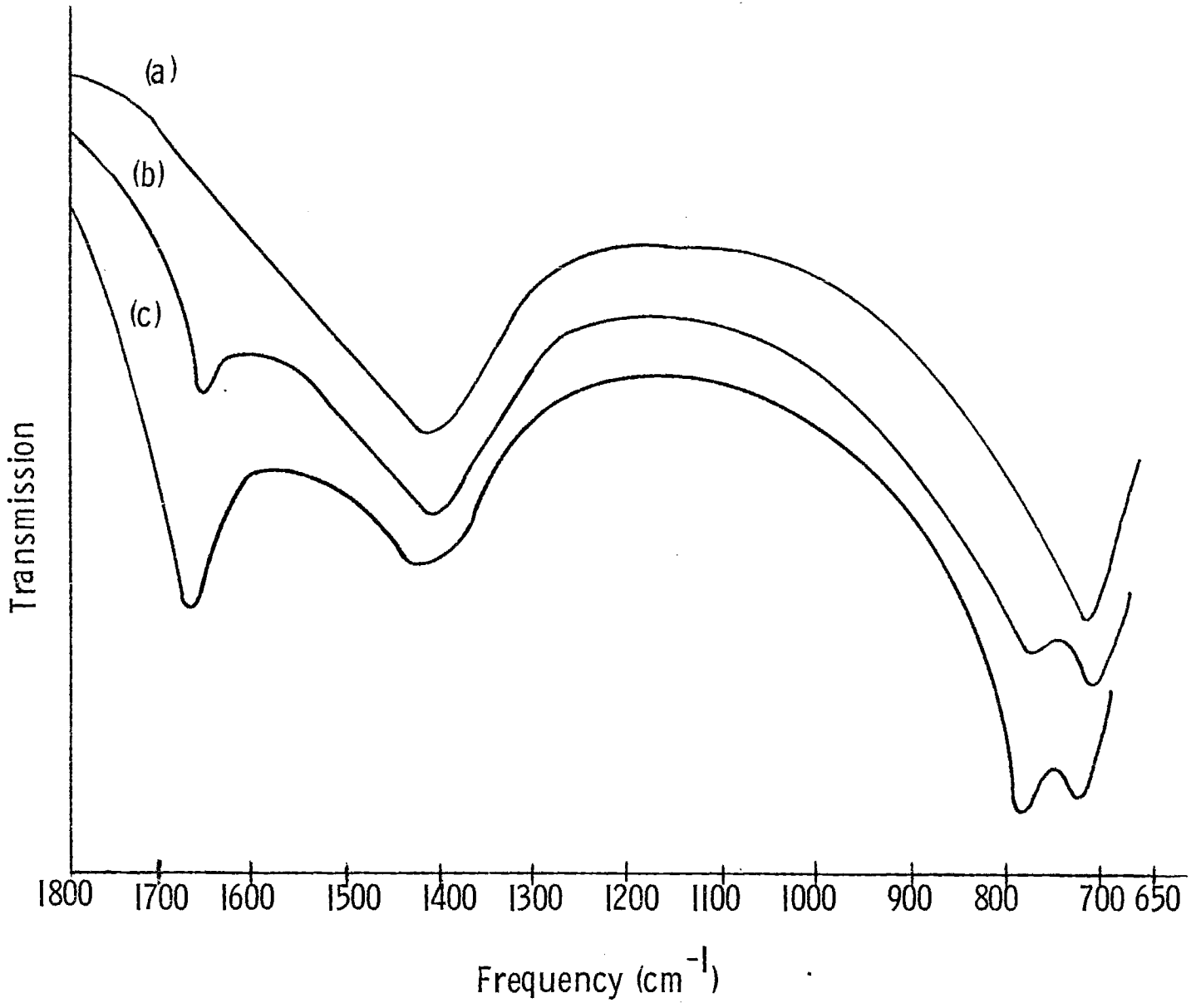

(a)
(b)
(c)
Transmission
1800
1600
1400
1200
1000
800
625
Frequency (cm^{-1})

Figure 3. Infrared spectra of solutions obtained by adding $LiAlH_4$ to $(CH_3)_2Zn$ in tetrahydrofuran. (a) 1:2 $LiAlH_4$ to $(CH_3)_2Zn$, (b) 2:3 $LiAlH_4$ to $(CH_3)_2Zn$ and (c) 1:1 $LiAlH_4$ to $(CH_3)_2Zn$.


(a)
(b)
(c)
Transmission
1800
1700
1600
1500
1400
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1200
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800
700
650
Frequency (cm^{-1})

Figure 4. Infrared spectra of solutions obtained by adding $(CH_3)_2Zn$ to $LiAlH_4$ in tetrahydrofuran. (a) $LiZnMe_2AlH_4$; (b) $LiZn_2Me_4AlH_4$

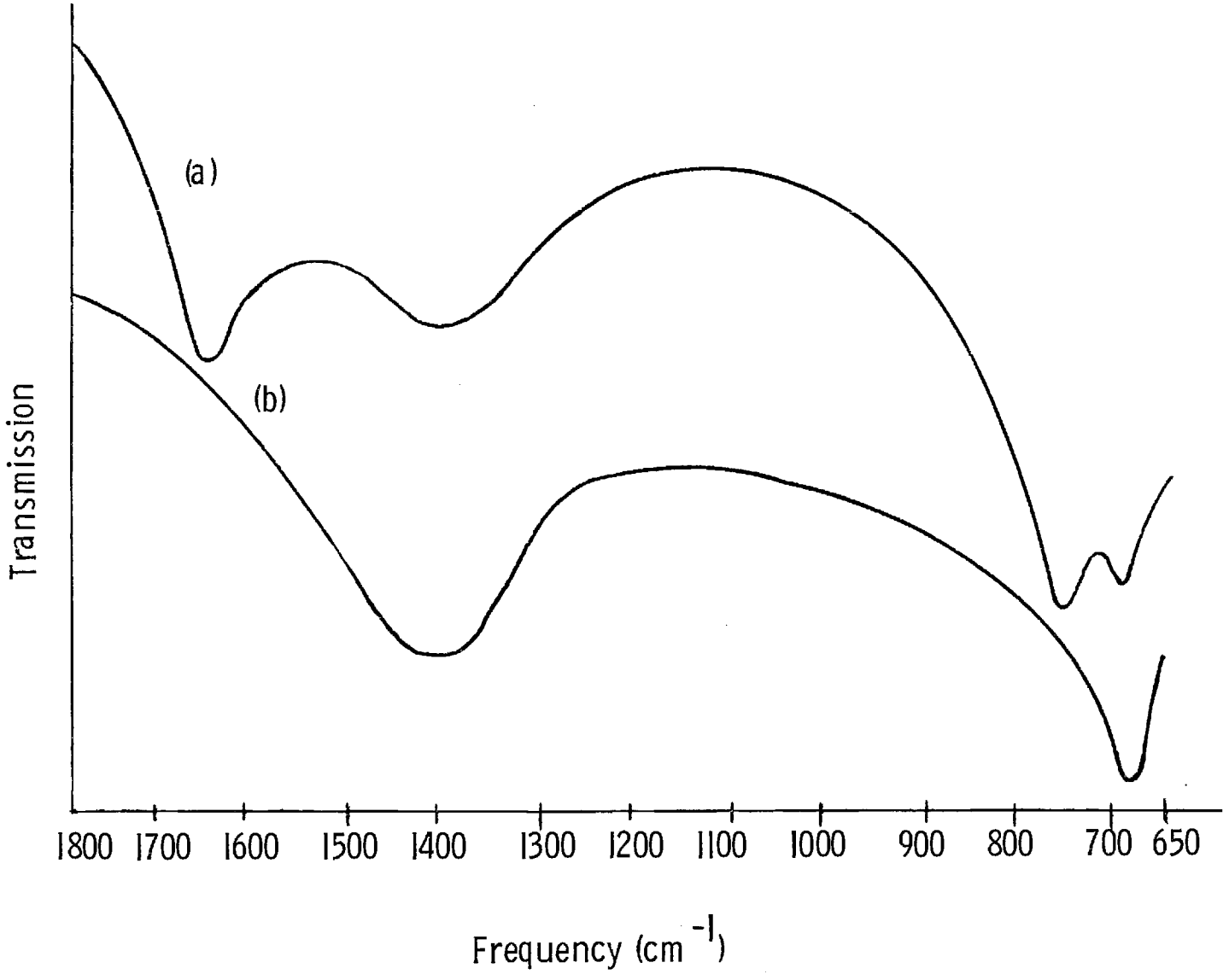
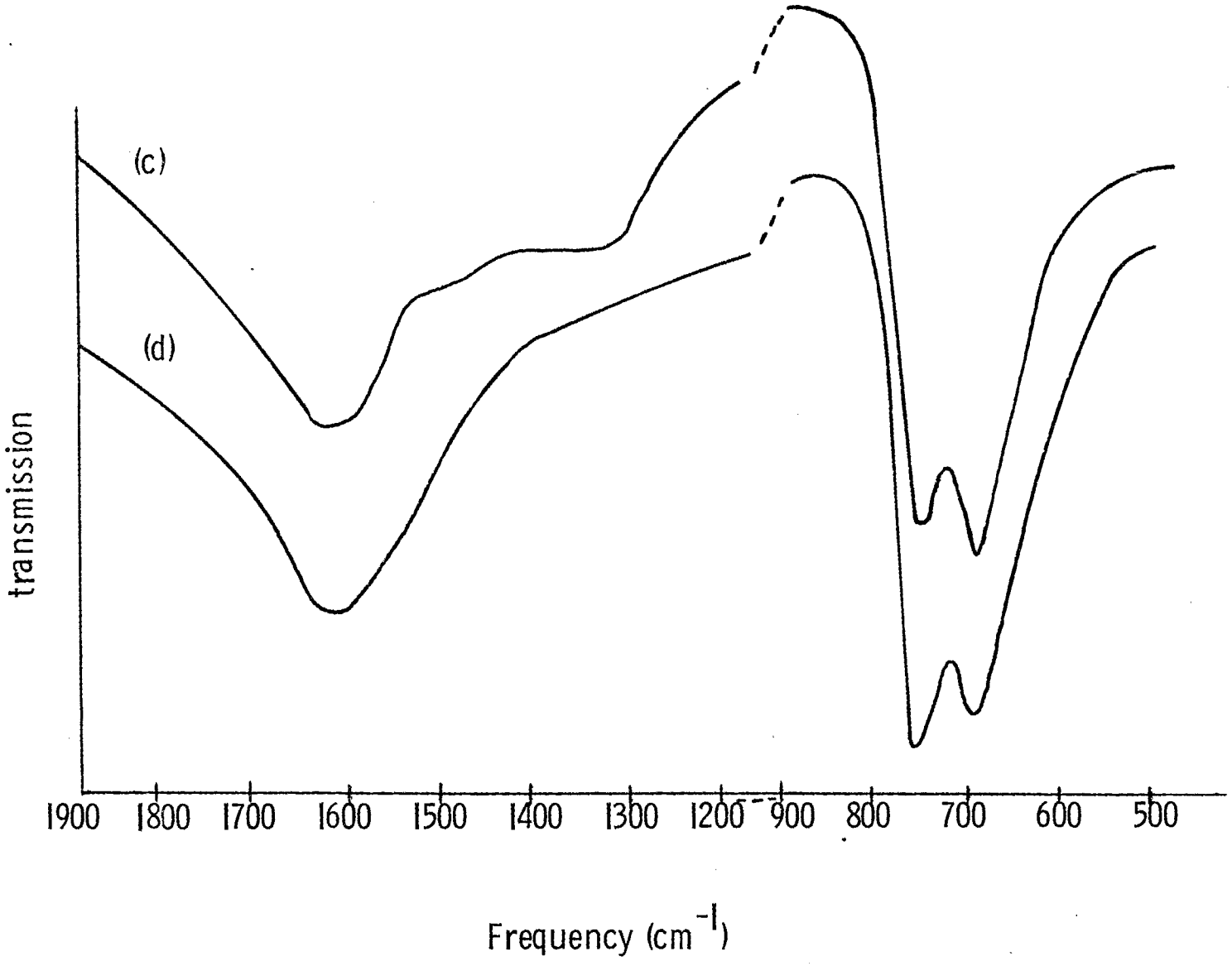

(a)
(b)
Transmission
1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 650
Frequency (cm -1)

Figure 5. Infrared spectra of $NaZn(CH_3)_2H$ and THF soluble products from its reaction with AlH_3. (a) $(CH_3)_2Zn$ in THF, (b) $NaZn(CH_3)_2H$ in THF, (c) $NaZn(CH_3)_2H + AlH_3$ in THF after 5 minutes and (d) $NaZn(CH_3)_2H + AlH_3$ in THF after 24 hours - $NaAl_2(CH_3)_4H_3$


(c)
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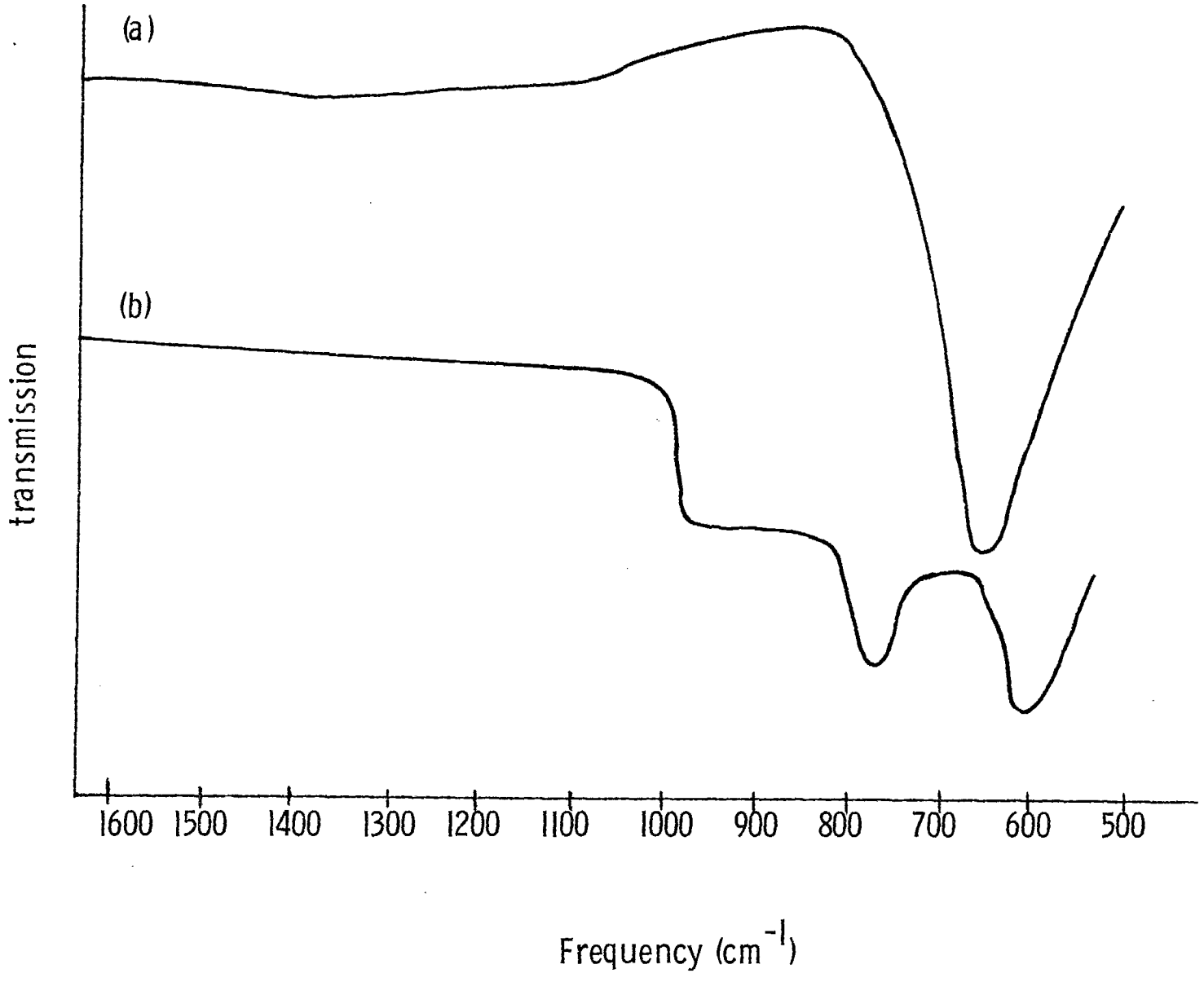
Frequency (cm^{-1})


(a)
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Frequency (cm^{-1})

Figure 6. Infrared spectra of (a) $NaZn_2(CH_3)_4H$ and (b) $NaZn_2(CH_3)_4AlH_4$

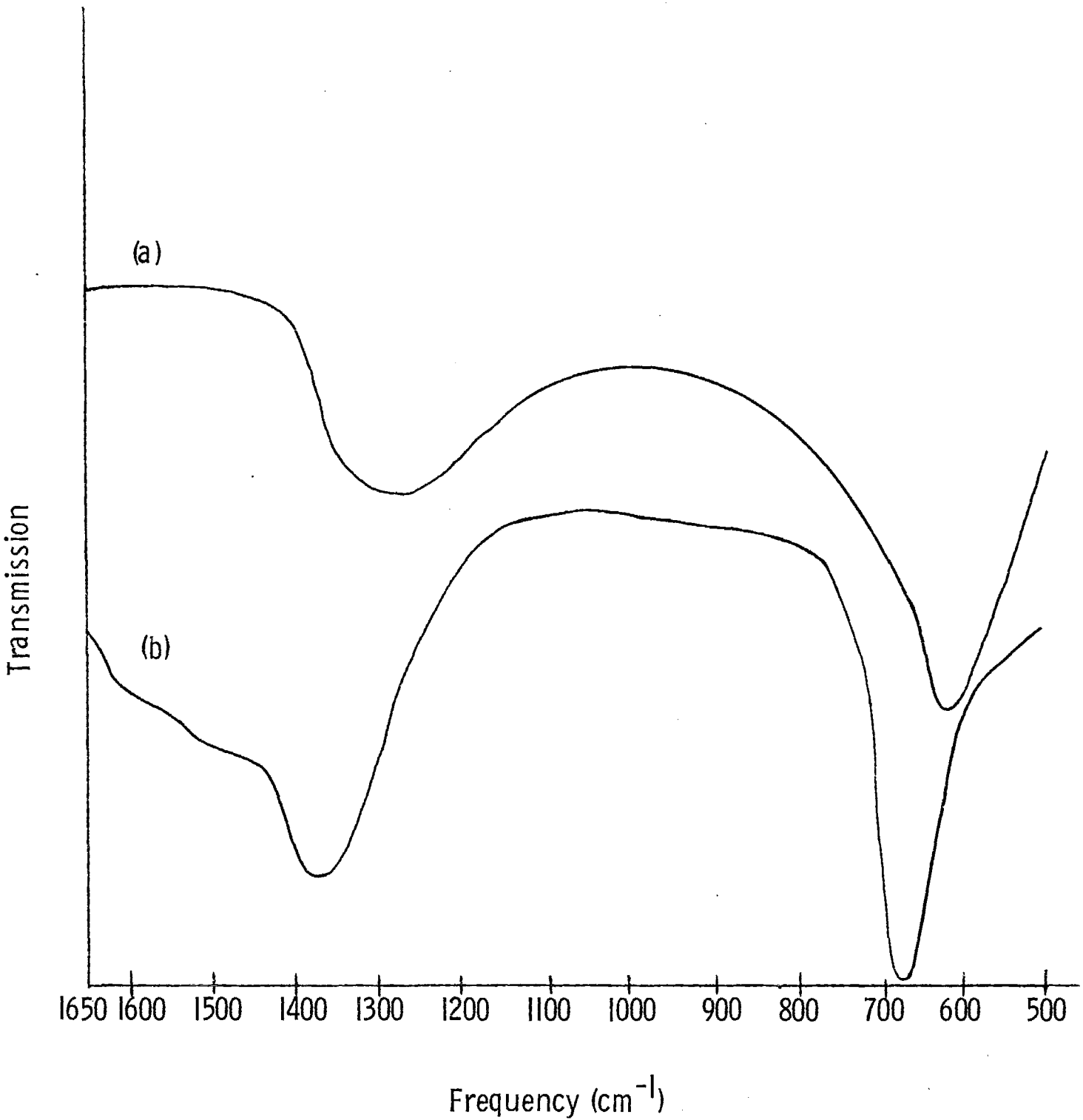
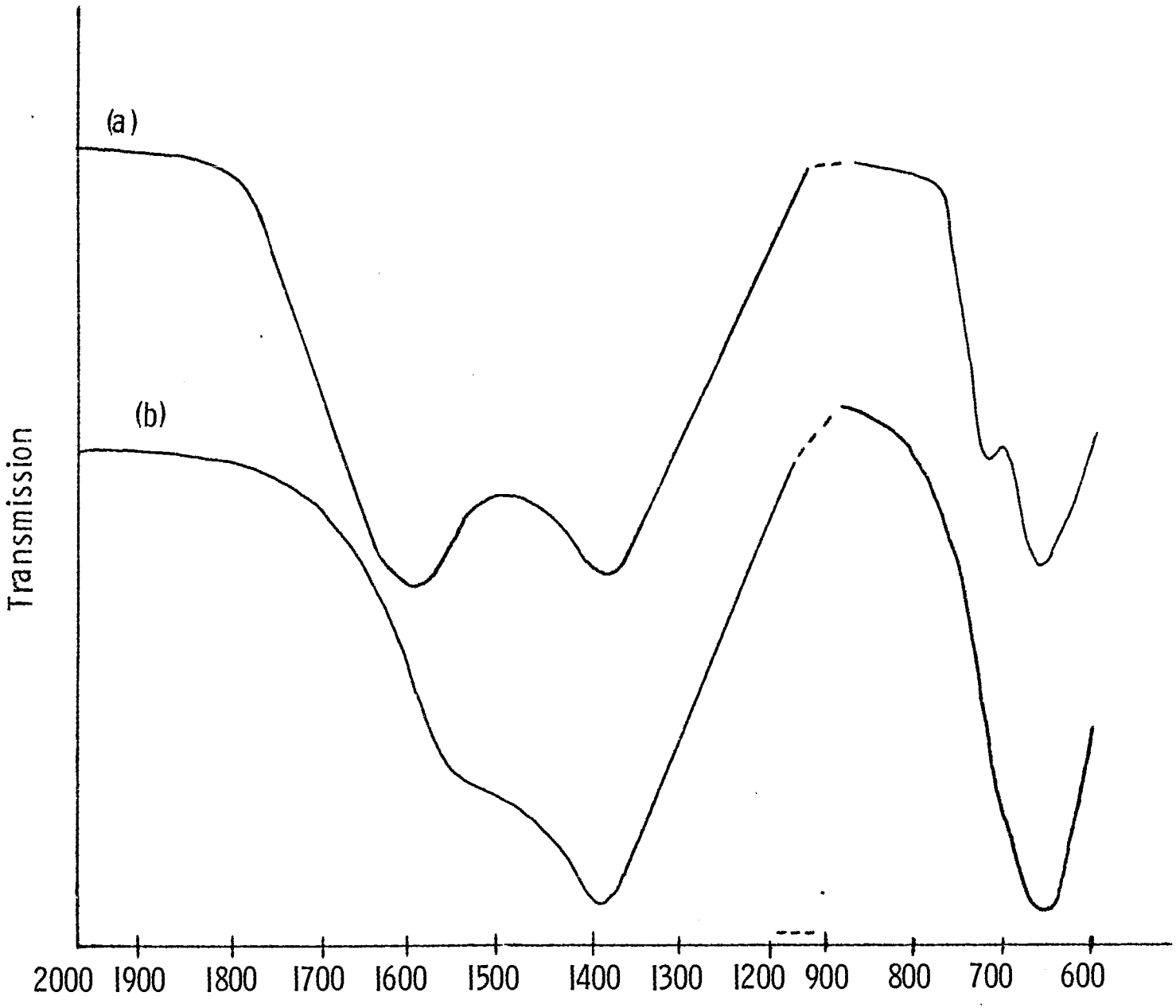

(a)
(b)
Transmission
1650 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500
Frequency (cm^{-1})

Figure 7. Infrared spectra of solutions obtained when $(CH_3)_2Zn$ was added to $NaAlH_4$ in tetrahydrofuran (a) $NaAlH_4$ to $(CH_3)_2Zn$, 1:1 (b) 1:2


(a)
(b)
Transmission
2000
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1800
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1600
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1400
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900
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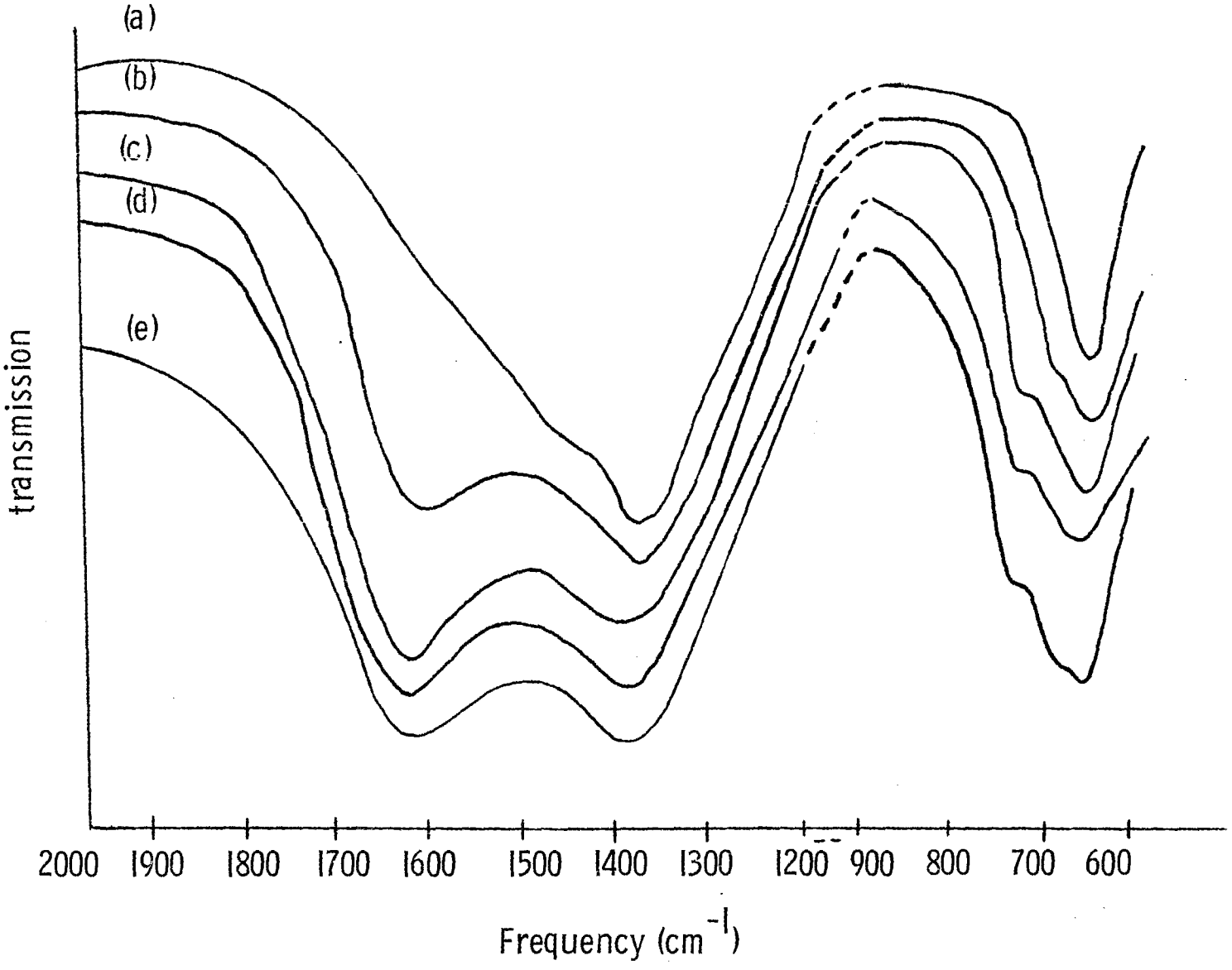
700
600

Figure 8. Infrared spectra of solutions obtained by adding $NaAlH_4$ to $(CH_3)_2Zn$ in tetrahydrofuran. (a) 1:2 $NaAlH_4$ to $(CH_3)_2Zn$ (b) 2:3 $NaAlH_4$ to $(CH_3)_2Zn$, (c) 1:1 $NaAlH_4$ to $(CH_3)_2Zn$ after 5 minutes, (d) 1:1 $NaAlH_4$ to $(CH_3)_2Zn$ after 2.5 hours, (e) 1:1 $NaAlH_4$ to $(CH_3)_2Zn$ after 28 hours, (f) 1:1 $NaAlH_4$ to $(CH_3)_2Zn$ after 4 days and (g) 1:1 $NaAlH_4$ to $(CH_3)_2Zn$ after 7 days


(a)
(b)
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(d)
(e)
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1400
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600
Frequency (cm⁻¹)

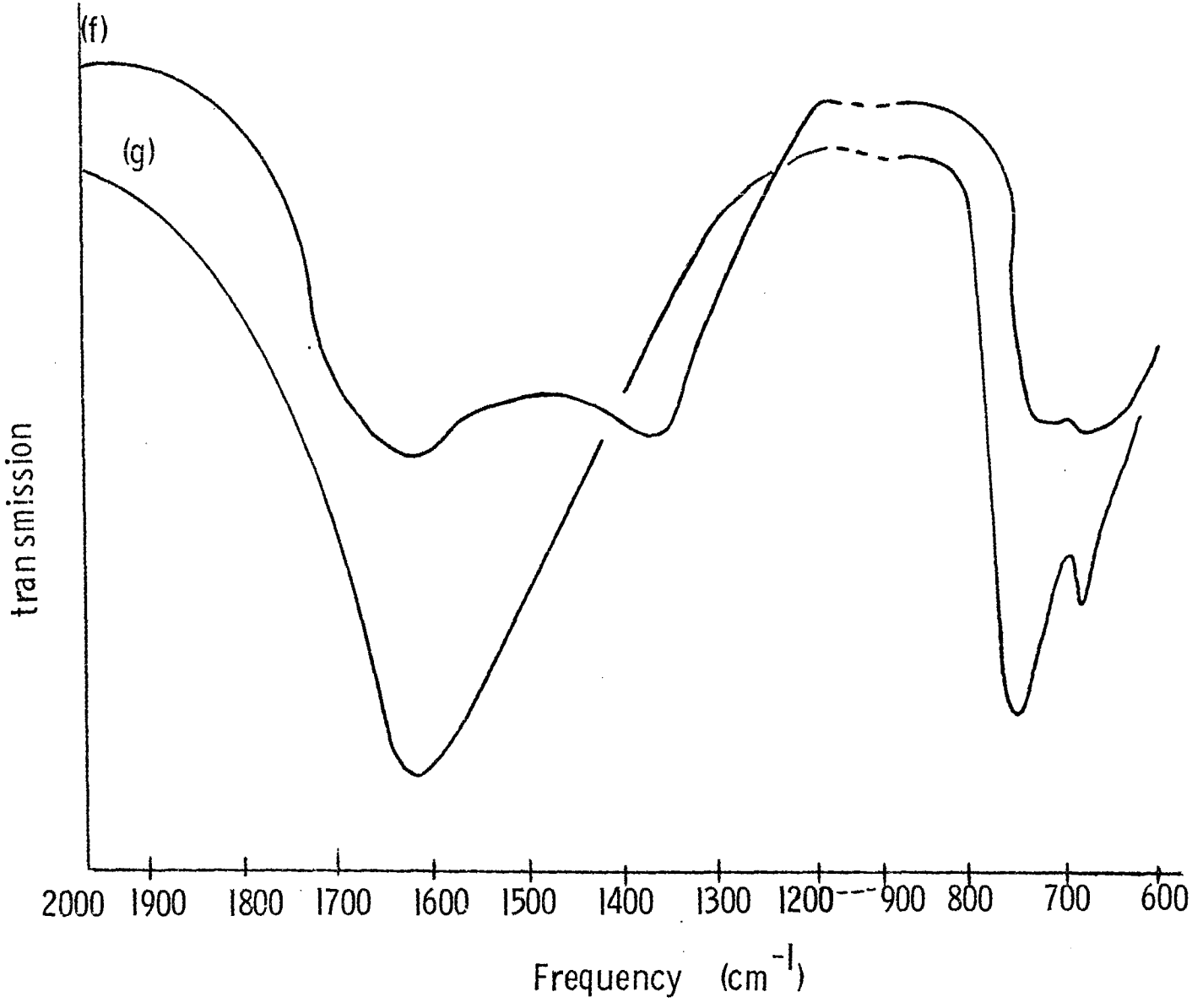
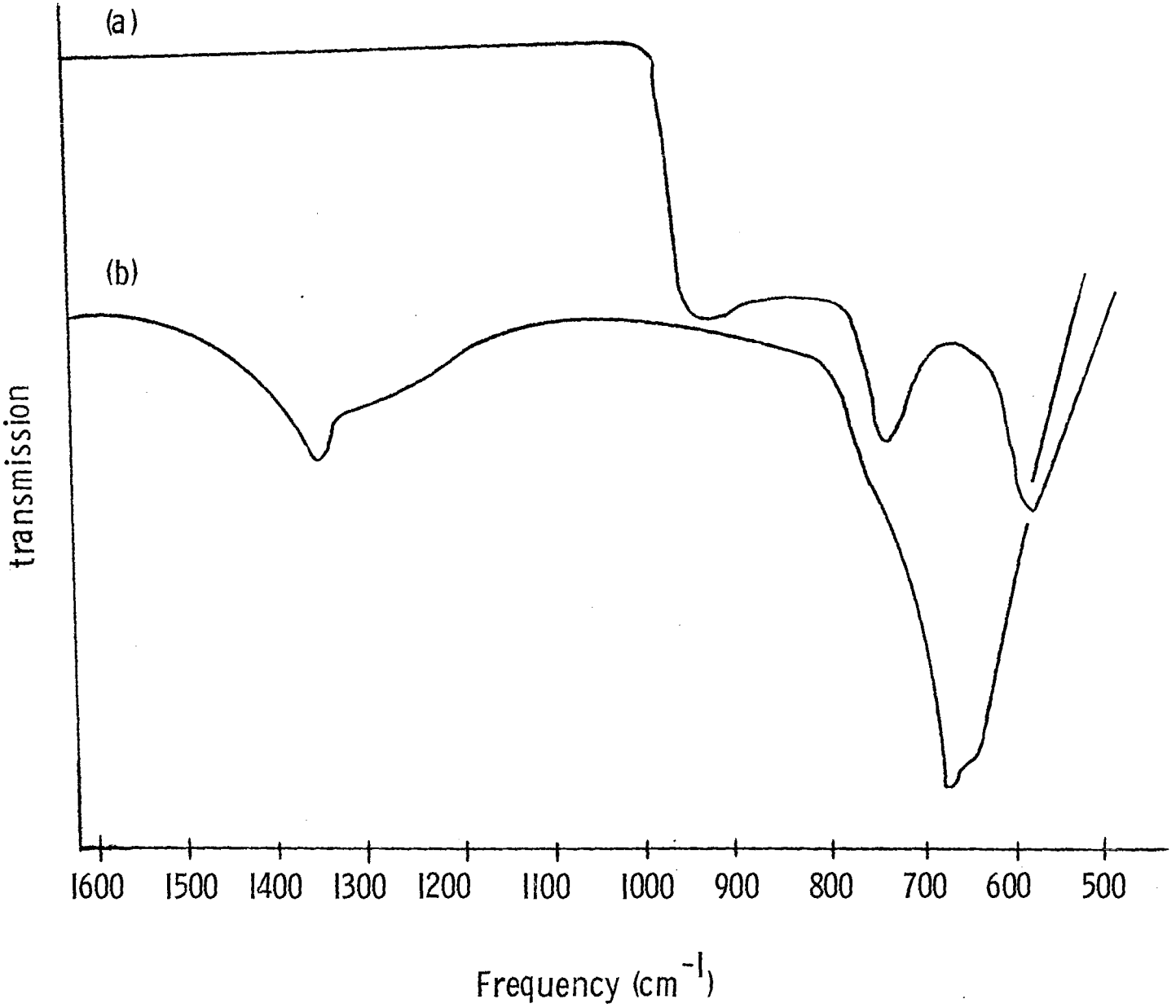

(f)
(g)
transmission
2000 1900 1800 1700 1600 1500 1400 1300 1200 900 800 700 600
Frequency (cm⁻¹)

Figure 9. Infrared spectra of $KZn(CH_3)_2H$, THF products from its reaction with AlH_3, and the products from the reaction of $KAlH_4$ with $(CH_3)_2Zn$ in tetrahydrofuran.

(a) $KZn(CH_3)_2H$ in THF, (b) 1:1 $KAlH_4$ + $(CH_3)_2Zn$ after 3 minutes, (c) 1:1 $KZn(CH_3)_2H$ to AlH_3 after 3 hours and (d) 1:1 $KAlH_4$ + $(CH_3)_2Zn$ after 3 hours


(a)
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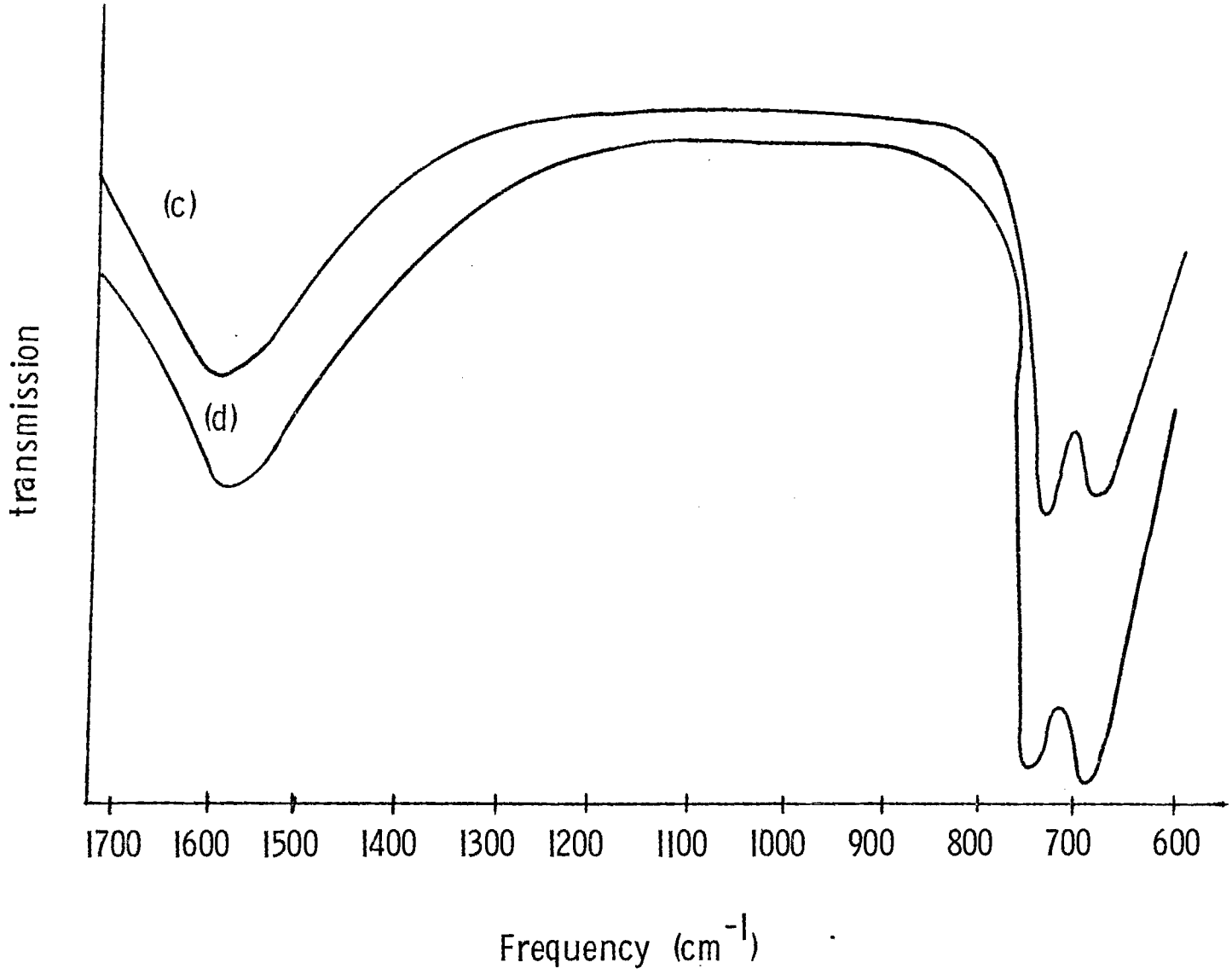
Frequency (cm^{-1})


(c)
(d)
transmission
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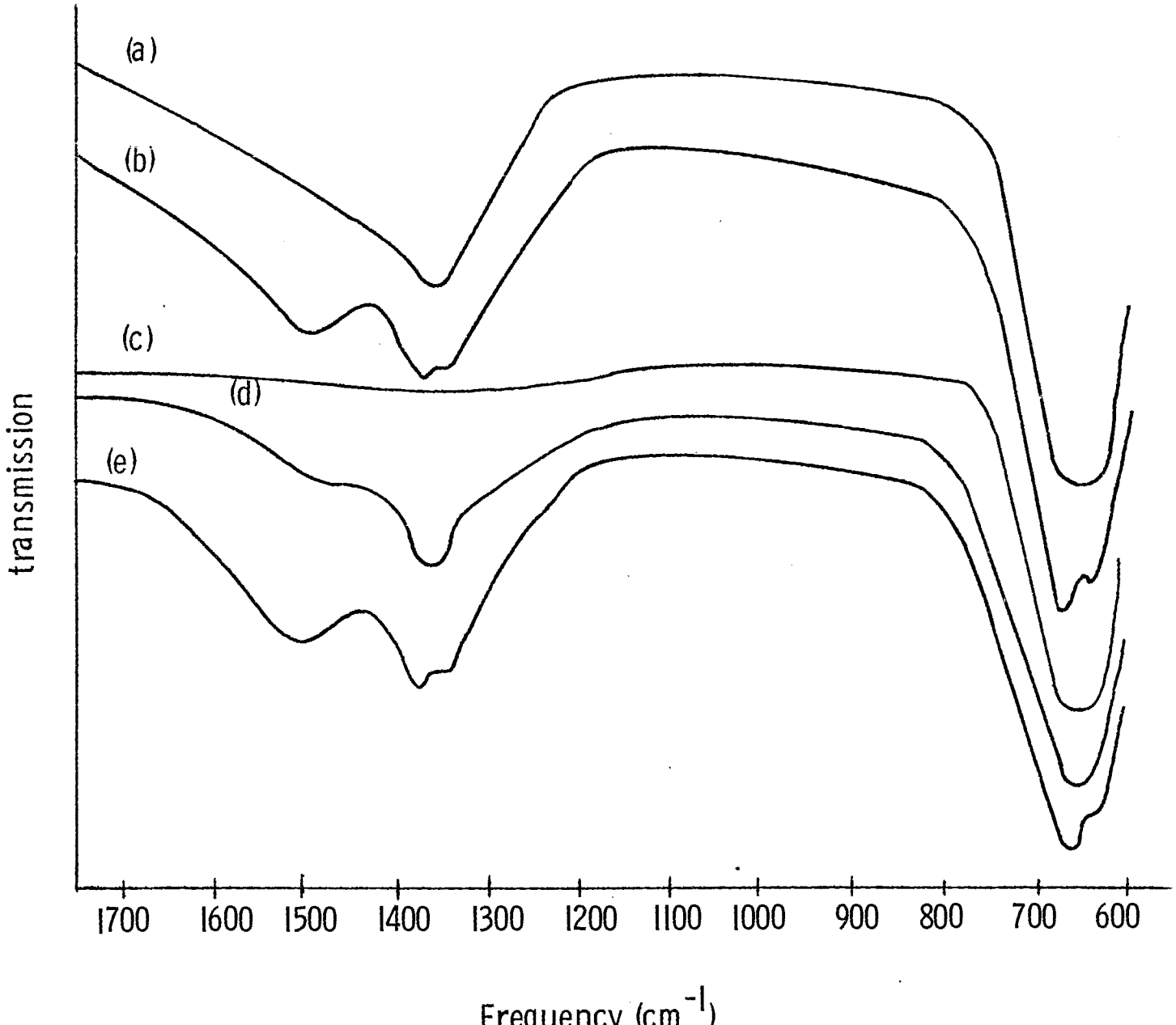
700
600
Frequency (cm^{-1})

Figure 10. Infrared spectra of $KZn_2(CH_3)_4H$, products from the reaction of $KAlH_4$ with $(CH_3)_2Zn$ in 1:2 ratio, and products from the reaction of $KZn_2(CH_3)_4H$ with AlH_3 in tetrahydrofuran. (a) 1:2 $KAlH_4$ to $(CH_3)_2Zn$ after 5 minutes, (b) 1:2 $KAlH_4$ to $(CH_3)_2Zn$ after 20 minutes, (c) 1:2 $KAlH_4$ to $(CH_3)_2Zn$ after 4 hours, (d) 2:1 $KZn_2(CH_3)_4H$ to AlH_3 and (e) 1:1 $KZn_2(CH_3)_4$ to AlH_3 after 5 minutes. (f) 1:1 $KZn_2(CH_3)_4H$ to AlH_4 after 4 hours, (g) 1:2 $KZn_2(CH_3)_4H$ to AlH_3 $(Al(CH_3)_2H)$ and (h) $KZn_2(CH_3)_4H$


(a)
(b)
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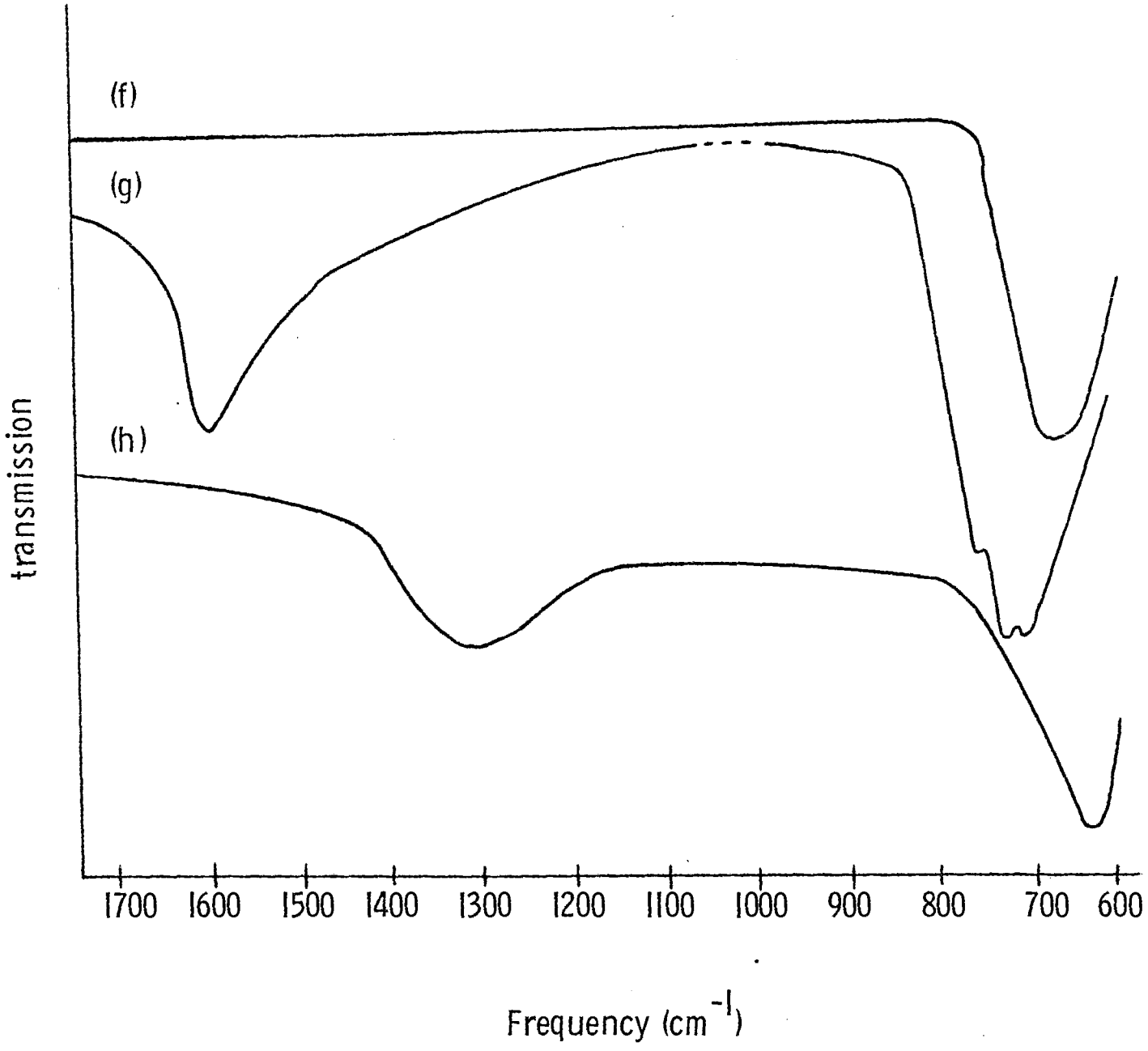
Frequency (cm^{-1})


(f)
(g)
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transmission
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1400
1300
1200
1100
1000
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600
Frequency (cm^{-1})

[Reprinted from Inorganic Chemistry, 12, 2860 (1973).]

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Study of the Reactions of Lithium Aluminum Hydride and Sodium Aluminum Hydride with Beryllium Chloride in Diethyl Ether and Tetrahydrofuran. A Report Questioning the Existence of $Be(AlH_4)_2$ in Solution

C. ASHBY,* J. R. SANDERS, P. CLAUDY, and R. D. SCHWARTZ

Received May 11, 1973

The reactions of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ were studied in 1:1 and 2:1 ratios in both diethyl ether and THF as solvents. No evidence for the previously reported $Be(AlH_4)_2$ was found. In 2:1 ratio the reaction of $NaAlH_4$ and $BeCl_2$ in THF was found to be similar to the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether. Two surprising aspects of the latter reaction are that the AlH_3 formed is soluble in diethyl ether and the (2 LiCl)-BeH_2 formed is actually isolated as a complex ($Li_2BeH_2Cl_2$). The reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in THF results in complete solubilization of all products.

$$2NaAlH_4 + BeCl_2 \xrightarrow{THF} 2NaCl\downarrow + BeH_2\downarrow + 2AlH_3$$

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3$$

Once again $Li_2BeH_2Cl_2$ and AlH_3 are formed as in diethyl ether; however, in THF $Li_2BeH_2Cl_2$ is soluble. Evidence is presented to support the equilibrium $2LiAlH_4 + BeCl_2 \rightarrow Li_2BeH_2Cl_2 + 2AlH_3 \rightleftharpoons LiAlH_3Cl + LiBeH_2Cl + AlH_3$. The reaction of $LiAlH_4$ with $BeCl_2$ in 1:1 ratio in diethyl ether and that of $NaAlH_4$ with $BeCl_2$ in 1:1 ratio in THF present a similar picture since the by-products LiCl and NaCl are insoluble in diethyl ether and THF, respectively. Independent evidence has

$$2LiAlH_4 + 2BeCl_2 \xrightarrow{Et_2O} 2LiCl\downarrow + BeH_2\downarrow + HBeCl + H_2AlCl + AlH_3$$

$$2NaAlH_4 + 2BeCl_2 \xrightarrow{THF} 2NaCl\downarrow + BeH_2\downarrow + HBeCl + H_2AlCl + AlH_3$$

been obtained for the following reactions in order to establish the detailed nature of the above reactions

$$LiCl + AlH_3 \xrightarrow{THF} LiAlH_3Cl$$

$$2AlH_3 + BeCl_2 \xrightarrow{Et_2O} HBeCl + H_2AlCl + AlH_3$$

$$2LiCl + BeH_2 \xrightarrow[\text{or } Et_2O]{THF} Li_2BeH_2Cl$$

$$LiAlH_4 + HBeCl \xrightarrow{THF} LiBeH_2Cl + AlH_3$$

$$LiCl + HBeCl \xrightarrow{THF} LiBeCl_2H$$

Introduction

In 1951 Wiberg and Bauer[1] reported that the reaction of $LiAlH_4$ with $BeCl_2$ in diethyl ether yields beryllium aluminum hydride $Be(AlH_4)_2$ and LiCl (eq 1). The insoluble LiCl

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl \quad (1)$$

was reported to precipitate from solution leaving dissolved $Be(AlH_4)_2$ which was recovered by removal of solvent.

Wood and Brenner[2] using the method of Wiberg and Bauer[1] reported that metastable solutions of $Be(AlH_4)_2$ could be prepared by combining $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. It was reported that a white precipitate formed which was filtered from solution leaving a filtrate which exhibited a Be:Al:H ratio of 1.0:1.82:9.2, indicating the presence of $Be(AlH_4)_2$ in solution. The product was said to decompose within a few hours at the boiling point of ether; however, the decomposition products were not characterized. The product was reported to be stable for several days below 10°; however, the absence of data other than analysis leaves this product poorly described.

In other work,[3] the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether was reported to yield a precipitate of LiCl and BeH_2, leaving AlH_3 in solution.

Related to the work above is the reported preparation of $LiBe(AlH_4)_3$ which has been described in a recent patent.[4] This compound was prepared by the addition of $LiAlH_4$ in diethyl ether to a slurry of $BeCl_2$ in 2:1 ratio in a mixture of ether and hexane, at room temperature. Immediate precipitation resulted and the precipitated solid was removed as soon as the combination of reagents was completed. After addition of triethylamine to the filtrate, a solid having the empirical formula $LiBe(AlH_4)_3$ precipitated over a period of 7 days. The yield was *ca.* 5% based on $BeCl_2$. The compound was characterized by elemental and X-ray powder diffraction analysis. An explanation of the results obtained in this work was suggested (eq 2) based on prior art. If Be-

$$4LiAlH_4 + 2BeCl_2 \rightarrow [Be(AlH_4)_2 + BeCl_2 + 2LiAlH_4 + 2LiCl] \rightarrow LiBe(AlH_4)_3 + \tfrac{1}{2}BeH_2\downarrow + AlH_3 + \tfrac{1}{2}BeCl_2 + 3LiCl\downarrow \quad (2)$$

$(AlH_4)_2$ were formed initially and reacted preferentially with the $LiAlH_4$ reactant to form a stable adduct $[LiBe(AlH_4)_3]$, the complex might be isolated after removal of the insoluble

(1) E. Wiberg and R. Bauer, *Z. Naturforsch. B*, 6, 171 (1951).
(2) G. B. Wood and A. Brenner, *J. Electrochem. Soc.*, 104, 29 (1957).
(3) C. E. Holley and J. F. Lemons, "The Preparation of the Hydrides of Magnesium and Beryllium," Report 1A-1660, Los Alamos Scientific Laboratory, Los Alamos, N. M., April 1, 1954.
(4) G. Rice and R. Ehrlich, U. S. Patent 3,383,187 (May 14, 1968).

oducts. The addition of triethylamine to the product solution may serve to induce precipitation of the complex.

Recently we found in a study of reactions[5] of $LiAlH_4$ and $NaAlH_4$ with magnesium halides (where the halogen is Cl, Br, or I) in diethyl ether and tetrahydrofuran that halogen atoms were replaced in a stepwise fashion in a simple metathetical exchange process to yield first $XMgAlH_4$ and then $Mg(AlH_4)_2$. The nature of the products was controlled by the choice of halogen and the solvent type. The reaction of $NaAlH_4$ and $CaCl_2$ in 2:1 ratio was reported to yield $Ca(AlH_4)_2$ and NaCl.[6] On the other hand, reaction of zinc,[7] cadmium,[8] and mercury[9] halides with $LiAlH_4$ in diethyl ether or tetrahydrofuran produced only the insoluble, unstable binary hydrides ZnH_2, CdH_2, and HgH_2 which decomposed to the metal and hydrogen at or below room temperature. It was postulated that $M(AlH_4)_2$ was initially formed which rapidly decomposed to the group IIb metal hydride which precipitated and to AlH_3 which remained in solution.

$$M(AlH_4)_2 \rightarrow MH_2 + 2AlH_3 \quad (M = Zn, Cd) \tag{3}$$

Recent Russian work[9] reported the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ in diethyl ether according to eq 4 and 5. The

$$2LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \tag{4}$$

$$3LiAlH_4 + BeCl_2 \rightarrow LiAl_3H_{10} + BeH_2 + 2LiCl \tag{5}$$

compounds $LiAl_2H_7$ and $LiAl_3H_{10}$ were reported to be very unstable in ether but somewhat more stable in the solid state.

Since there are conflicting reports concerning the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether, this reaction was reexamined in an attempt to resolve the conflicting reports. The reaction of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in tetrahydrofuran solvent was also studied. Using elemental analysis, infrared spectroscopy, and X-ray powder diffraction techniques the above reactions were studied in detail.

Experimental Section

Reagents. Beryllium metal was obtained from the Brush Beryllium Co., Elmore, Ohio; the metal was in the form of high-purity electrorefined flake (99.4%). Chlorine gas was Matheson high purity, used without further purification. Bromine was obtained from Dow Chemical Co. and used without further purification. All solvents were distilled at atmospheric pressure from $LiAlH_4$ (diethyl ether) or $NaAlH_4$ (benzene, tetrahydrofuran) immediately before use. $LiAlH_4$ and $NaAlH_4$ were obtained as gray, lumpy solids from Ventron, Metal Hydrides Division.

Instrumentation. Infrared spectra were obtained using either a Perkin-Elmer Model 621 or a Model 257 infrared spectrophotometer. Potassium bromide cells were used. Spectra of solids were obtained in Nujol which had been dried over sodium wire and stored in a drybox.

X-Ray powder diffraction patterns were obtained using a Debye–Scherrer camera of 114.6-mm diameter using Cu Kα radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used.

Thermal analysis was performed on a Mettler Thermoanalyzer II modified for differential pressure recording at reduced pressure. Samples of approximately 50-mg size were run in an aluminum crucible at a heating rate of 2°/min. Alumina (60 mesh) was used as the reference material. In the part labeled ΔP on the dta–tga tracer, the shaded area indicates that a condensable gas only is being evolved. A more detailed description of the apparatus has been described elsewhere.[10]

Analytical Work. Aluminum was determined by standard EDTA titration. Beryllium was determined gravimetrically by precipitation as the hydroxide, followed by ignition to the oxide at 1000° for 1 hr. Aluminum interference was prevented by the addition of an excess of EDTA which complexes the aluminum and prevents its precipitation as the hydroxide. An alternative method used for determining beryllium and aluminum was to adjust the pH of the sample to 7.8 and then add NaF. This sample was heated to dissolve the NaF. When the sample was cooled, the NaOH formed was titrated to pH 7.8 with standard HCl.

Analysis for chloride and bromide was carried out using a modified Volhard procedure.

Hydrogen analysis was accomplished by acid hydrolysis of a weighed amount of sample on a standard vacuum line equipped with a Toepler pump.[11]

Preparative Methods. All operations were carried out under an atmosphere of dry, oxygen-free nitrogen in a glove box or by use of bench-top inert-atmosphere techniques.[11]

Standard Solutions of Complex Aluminum Hydrides. Solutions of $LiAlH_4$ in diethyl ether and tetrahydrofuran and solutions of $NaAlH_4$ in tetrahydrofuran were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. These reactant solutions were standardized by aluminum analysis and transferred volumetrically.

Beryllium Chloride Solvates. Beryllium chloride was prepared according to the method of Wood and Brenner.[2] Argon was used as a carrier gas instead of nitrogen, resulting in an almost quantitative yield of $BeCl_2$. To prepare the etherates of $BeCl_2$, a quantity of the unsolvated halide was suspended in dry benzene and the mixture cooled in an ice–water bath. A quantity (50% excess based on the bis solvate) of dry diethyl ether or tetrahydrofuran was added slowly as the mixture was stirred. The solvated $BeCl_2$ which is soluble in benzene was isolated by removal of benzene under vacuum. *Anal.* Calcd for $BeCl_2 \cdot 2THF$: Be, 4.02; Cl, 31.6. Found: Be, 3.93; Cl, 30.9. Calcd for $BeCl_2 \cdot 2Et_2O$: Be, 3.95; Cl, 31.1. Found: Be, 3.86; Cl, 30.5. Infrared and X-ray powder diffraction data were recorded for the solvates.

Reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 Ratio in Ether. To 32.29 mmol of $BeCl_2$ in 250 ml of diethyl ether was added 64.58 mmol of $LiAlH_4$ solution at 0°. A white precipitate formed at once and increased in volume as the $LiAlH_4$ was added. The mixture was stirred for 15 hr and filtered through a glass frit, yielding a white residue and a colorless, clear filtrate. *Anal.* Found for the insoluble residue: H, 2.64; Be, 7.72; Al, 6.43; Cl, 60.6. The X-ray powder diffraction pattern contained only lines arising from LiCl. The infrared spectrum (Nujol mull) exhibited very broad absorptions at 1755, *ca.* 1350, and 768 cm^{-1}. *Anal.* Found for the ether-soluble fraction: H, 5.99; Li, 0.73; Al, 50.2. No beryllium or chloride was detected. The solvent was removed under vacuum and the resulting solid was shown to contain no powder diffraction lines attributable to LiCl or starting materials. The infrared spectrum of a Nujol mull of this material showed the following absorptions: 1755 (s, vb), 1660 (s, vb), 1022 (s), 720 (s, b), and 605 (m) cm^{-1}.

A similar experiment was performed at −78°; the mixture was stirred at this temperature for 60 min and then filtered while cold. Again, a white residue was recovered, leaving a clear, colorless filtrate. *Anal.* Found for the insoluble residue: H, 2.40; Be, 7.50; Al, 8.55; Cl, 60.6. The infrared spectrum of a Nujol mull of the insoluble residue gave the following absorptions: 1750 (s, vb), 1350 (s, vb), 765 (m, vb), and 316 (s, b) cm^{-1}. The X-ray powder diffraction pattern indicated no lines other than those arising from LiCl. *Anal.* Found for the solid isolated by removing solvent from the ether-soluble fraction of this reaction: H, 5.98; Li, 0.78; Al, 50.2. Again, no beryllium or halogen was found. The infrared spectrum showed absorption bands at 1778 (s, vb), 1600 (s, vb), 1020 (s, b), 720 (s, b), and 597 (s, b) cm^{-1}. The X-ray powder diffraction pattern showed no lines attributable to LiCl or starting materials. Material balances in these reactions averaged 85–90%.

In a similar experiment in which the reaction temperature and time were different, 10 mmol of $BeCl_2$ was added to 20 mmol of $LiAlH_4$ in 150 ml of ether at room temperature. A white precipitate appeared immediately. The mixture was stirred for 2 hr and then filtered, yielding a white residue and a colorless clear filtrate. Removal of the solvent from the filtrate yielded a white powder. Analysis of the precipitate gave Be:Al:Li:H:Cl = 1.00:0.078:1.90:2.0:1.90. X-Ray analysis showed lines for LiCl plus another pattern (see Table III). The analysis of the soluble compound gave Be:Al:H:Li:Cl = 0.0:1.0:3.3:0.023:0.023.

The above reaction was repeated except the filtration was carried

(5) E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem.*, 9, 325 (1970).
(6) British Patent 905,985 (1962).
(7) E. Wiberg, W. Henle, and R. Bauer, *Z. Naturforsch. B*, 6, 393 (1951); 7, 249 (1952).
(8) E. Wiberg and W. Henle, *Z. Naturforsch. B*, 6, 461 (1951).
(9) T. N. Dymova, *et al.*, *Dokl. Akad. Nauk SSSR*, 184, 1338 (1969).
(10) (a) E. C. Ashby and J. Watkins, *Inorg. Chem.*, in press; (b) *J. Chem. Educ.*, in press.
(11) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapter 7.

at 2–3 min after the mixing of the reactants. The analysis of the precipitate gave Be:Al:H:Li:Cl = 1.0:0.109:2.1:2.2:2.2. X-Ray analysis gave two fine lines characteristic of LiCl plus another pattern which corresponds to that found in the precipitate above except with more lines. The dta-tga is shown in Figure 1. The analysis of the soluble compound gave Al:H:Li:Be = 1.0:2.97:0.002:0.0. The dta-tga is shown in Figure 2. The precipitate was stirred in diethyl ether for 3 days at room temperature. At the end of this time the ether was removed under vacuum. The X-ray powder pattern showed only lines characteristic of LiCl. The dta-tga is shown in Figure 3 (compare it to Figure 1).

Equilibration of a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in diethyl ether for 135 hr at 25° yielded products with infrared spectra identical with those of the products isolated when the reaction mixture was worked up immediately. The X-ray powder pattern of the insoluble product exhibited only lines characteristic of LiCl.

Reaction of $NaAlH_4$ and $BeCl_2$ in 2:1 Ratio in Tetrahydrofuran. To a stirred suspension of 20.87 mmol of $BeCl_2 \cdot 2THF$ in 150 ml of THF, cooled to 0° in an ice-water bath, was added 41.74 mmol of $NaAlH_4$ in THF. Immediate precipitation resulted. After stirring for 30 min at 0°, the mixture was filtered while cold yielding a white residue and a clear, colorless filtrate. Removal of the THF from the filtrate at reduced pressure produced a white solid. *Anal.* Found for the insoluble fraction: H, 1.36; Be, 5.16; Al, 1.91; Cl, 46.9. The X-ray powder diffraction pattern contains five unidentified lines in addition to those arising from NaCl. The infrared spectrum of a Nujol mull of this sample exhibits the following absorptions: 1710 (s, vb), 1350 (s, vb), 1020 (w), and 815 (s, vb) cm^{-1}. *Anal.* Found for the residue from the soluble fraction: H, 3.05; Be, 0.309; Al, 26.2; Cl, 0.763. The X-ray powder diffraction pattern of this sample had many lines, but none due to $BeCl_2 \cdot 2THF$. The infrared spectrum of a Nujol mull shows absorptions at the following positions: 1800 (s, b), 1625 (m, vb), and 1015 (s, b) cm^{-1}.

This reaction was repeated and the products were stirred at room temperature for a period of time to allow possible product redistribution. To 10.39 mmol of $BeCl_2 \cdot 2THF$ in 75 ml of THF was added 20.77 mmol of $NaAlH_4$. The reaction was carried out at room temperature producing an immediate white precipitate. After stirring for 92 hr no obvious further solubilization of the precipitate had occurred. Filtration of this mixture produced a white solid and a colorless filtrate. Infrared examination of the filtrate showed the following absorptions (THF bands deleted): 1640 (s), 793 (s), and 726 (s) cm^{-1}. Nmr spectra of the filtrate indicated nothing other than solvent over a 950-Hz sweep width. Removal of solvent from this filtrate yielded a white solid. *Anal.* Found: H, 3.39; Be, 3.70; Al, 25.6; Cl, 2.59. A Nujol mull of this solid showed infrared absorption bands at 1816 (s, b), 1606 (s, vb), 1350 (m, b), 1170 (w), 1120 (w), 1017 (w), 969 (w), 846 (w), 740 (m, b), and 671 (w) cm^{-1}. The X-ray powder diffraction pattern of this solid consists of four lines also found in the product resulting by removing solvent from the reaction mixture of 2 $LiAlH_4$ + $BeCl_2$ in THF. *Anal.* Found for the insoluble residue obtained from this reaction: H, 0.649; Be, 2.77; Al, 1.80; Cl, 44.2. The infrared spectrum of a Nujol mull of this solid had the following absorptions: 1805 (s, b), 1683 (s, b), 1544 (s, b), 1322 (m, sh), 1238 (w), 1150 (m), 1058 (m, sh), 1029 (s), 986 (m), 967 (m), 855 (s, b), 764 (s, b), and 723 (s, b) cm^{-1}. The X-ray powder diffraction pattern contains the NaCl pattern plus a faint, indistinct line found in the pattern observed above for the soluble portion.

An attempt was made to detect the presence of butoxyalane species (produced by AlH_3 cleavage of THF) in the soluble 2:1 product which had been equilibrated for 92 hr. Acid hydrolysis of the solid, followed by benzene extraction of the hydrolysate, confirmed the presence of 1-butanol when the extract was examined by vapor-phase chromatography. The estimated aluminum:butanol ratio was slightly greater than 1.

The above reaction was repeated for a shorter reaction period in order to minimize THF cleavage. To 9.95 mmol of $BeCl_2$ as a suspension in THF was added 19.9 mmol of $NaAlH_4$ in THF. The mixture was stirred for 1.5 hr and filtered. A white precipitate and slightly turbid solution were obtained. The solvent was removed from the filtrate under vacuum producing a white powder. Analysis of the precipitate gave a Be:H:Cl:Na:Al ratio of 1.2:1.96:2.93:2.30:0.04. The X-ray powder pattern of this solid showed lines for NaCl plus two lines which do not match $BeCl_2 \cdot 2THF$. The analysis of the THF-soluble portion gave a Na:Al:H:Be:Cl ratio of 0.15:1.00:2.98:0.0:0.0.

Reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 Ratio in THF. To 32.1 mmol of $BeCl_2 \cdot 2THF$ suspended in 200 ml of dry THF was added 64.2 mmol of $LiAlH_4$. No heat of reaction was noted, but most of

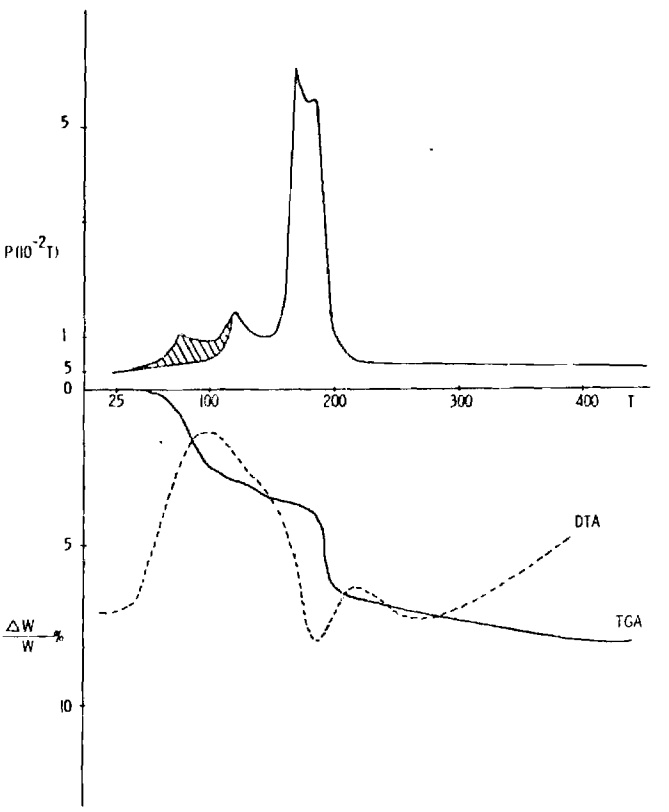


Figure 1. Vacuum dta-tga of $BeH_2 \cdot 2LiCl$.

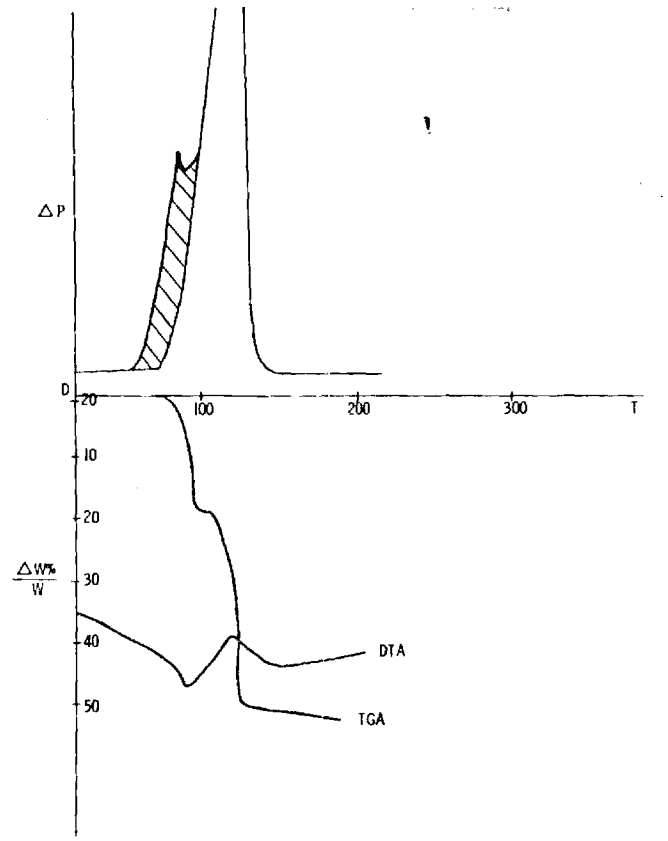


Figure 2. Vacuum dta-tga of $AlH_3 \cdot 0.25OEt_2$.

the suspended halide dissolved immediately leaving a slightly turbid solution. Stirring at 25° for 48 hr produced a completely clear, colorless, homogeneous solution. Removal of solvent until the volume was 100 ml caused no change. Approximately 100 ml of dry benzene was distilled into the solution, causing the appearance of a white precipitate. After removal of 50 ml of solvent by reduced pressure distillation, the solution was filtered to separate the white

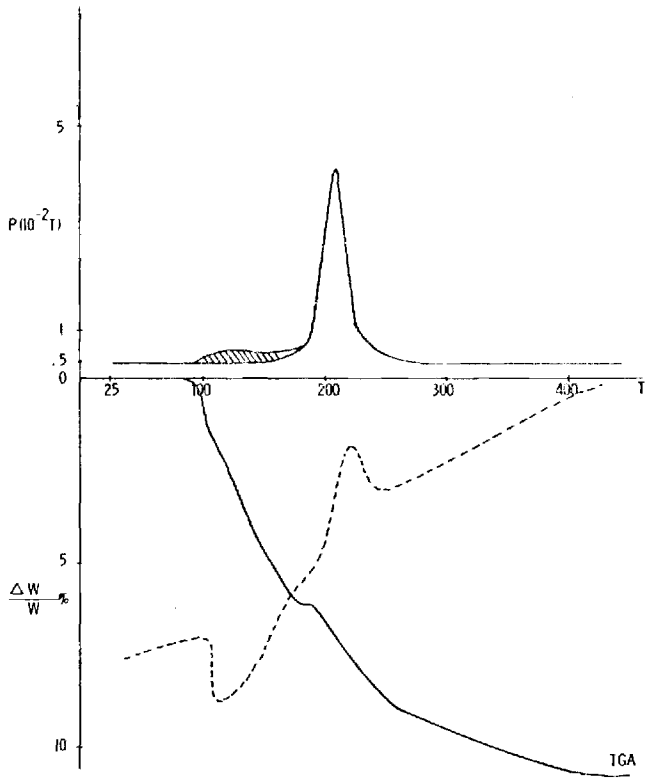


Figure 3. Vacuum dta–tga of a mixture of 2 LiCl + BeH_2.

insoluble residue from the clear filtrate. The residue was shown to be pure LiCl (26 mmol, 40%) by infrared and powder diffraction examination. Evaporation of the remainder of the solvent produced a gummy residue which solidified. The X-ray powder diffraction pattern of this solid showed the presence of additional LiCl plus nine other weak lines which could have arisen from a trace of $BeCl_2 \cdot 2THF$ or $LiAlH_4 \cdot n$THF. The infrared spectrum of a Nujol mull of this material showed the following absorption pattern: 1802 (s), 1023 (m), 842 (m), 752 (s), 725 (s), 623 (w), and 528 (w) cm^{-1}. Readdition of 100 ml of benzene to the product, followed by vigorous stirring, caused dissolution of some of the solid material. Filtration yielded a white residue and a colorless filtrate. The X-ray powder diffraction pattern of the white solid indicated the presence of LiCl plus lines found in the original sample before benzene addition. The infrared spectrum of this solid showed the following absorptions: 1812 (s, b), 1616 (s, vb), 1236 (m, b), 1071 (m), 1028 (m), 859 (m), 843 (m), 753 (s), 605 (s), and 534 (s) cm^{-1}. Removal of benzene solvent from the filtrate produced a gummy solid which would not solidify after prolonged pumping at 10^{-5} mm pressure, and for which no diffraction data could be obtained. The infrared spectrum of a Nujol mull of this material was the same as that found for the original material before benzene addition, with the appearance of a broad band of low intensity at 1619 cm^{-1}. *Anal.* Found for the benzene-insoluble portion of this reaction: H, 1.86; Al, 17.0; Cl, 37.4. Found for the benzene-soluble product: H, 1.68; Be, 4.47; Al, 16.6; Cl, 1.88.

The above reaction was repeated under conditions designed to minimize solvent cleavage. To 12.37 mmol of $BeCl_2 \cdot 2THF$ was added 24.74 mmol of $LiAlH_4$ in 225 ml of tetrahydrofuran. The reaction mixture temperature was maintained at 0° with vigorous stirring for 15 hr, producing a slightly turbid solution. The turbidity vanished when the mixture was stirred at room temperature for 2 hr. Solvent was removed by reduced pressure distillation at low temperature. The solution remained clear until a volume of 30 ml was reached, where a steadily increasing amount of solid began to precipitate. The final product was a white solid which was evacuated for 12 hr to remove excess solvent. The infrared spectrum of a Nujol mull of this material had the following absorptions: 1803 (s, b), 1616 (m, vb), 1017 (s), 852 (m), 750 (m), and 621 (m) cm^{-1}. The X-ray powder pattern of this solid contains LiCl lines plus other well-defined lines which match the corresponding sample from the previous reaction, with the exception of four weak lines.

The above reaction was repeated so that the residue isolated by solvent removal could be extracted with benzene. A white suspension resulted and filtration produced a white residue and a clear filtrate. The infrared spectrum of the insoluble residue exhibited the following absorptions: 1765 (s, b), 1350 (m, b), 1007 (w), 841 (w, b), 1718 (w), 669 (s), and 400–200 (s, b) cm^{-1}. Evaporation of benzene from the filtrate produced a white solid. *Anal.* Found: H, 3.19; Al, 28.5; Cl, 5.22. The beryllium concentration was too small to measure accurately and no lithium was found by flame photometric analysis. The infrared spectrum of this product had the following absorptions: 2000–1300 (b, s), 1169 (w), 1079 (m), 910 (w), 716 (w), 669 (w), and 246 (m) cm^{-1}.

In a separate experiment the solid obtained from the 2:1 reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether was added to a solution of AlH_3 in THF, such that the Be:Al ratio was 1.0:2.0. The solid dissolved and the infrared spectrum of the solution showed bands at 1740 (sh), 1700, 775, and 745 (sh) cm^{-1}. This corresponds to the spectrum of the reaction mixture from $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in THF. The infrared spectrum of $Li_2BeCl_2H_2$ in THF shows broad bands at 1825 (m) and 1650 (m) cm^{-1} and a sharper band at 775 cm^{-1}. If LiCl in THF is added to AlH_3 in THF in a 1:1 ratio, the infrared spectrum shows bands at 1740 (sh), 1700, 775, and 750 cm^{-1}.

Reaction of HBeCl and AlH_3 in THF. An equimolar mixture of BeH_2 and $BeCl_2$ in ether produced a clear solution from which HBeCl was produced on solvent removal. To the HBeCl was added AlH_3 in THF in a 1:1 ratio. No solid was formed. Analysis of the solution gave a Be:Al:H ratio of 1.15:1.00:4.14. The infrared spectrum of the solution gave bands at 1740, 800, and 740 cm^{-1}.

Reaction of $LiAlH_4$ and HBeCl in THF. To an ether solution of HBeCl was added $LiAlH_4$ in ether in a 1:1 ratio. A solid was formed and the infrared spectrum of the solution corresponded to AlH_3 in ether. When the solvent was removed under vacuum, a solid was produced which redissolved in THF. The infrared spectrum of the resulting solution showed bands at 1730 (sh), 1700, 775, and 740 cm^{-1}.

Reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 Ratio in THF. $LiAlH_4$ (28.9 mmol) was added dropwise to a stirred suspension of 28.9 mmol of $BeCl_2$ in 200 ml of tetrahydrofuran at 25°. The suspended crystals of $BeCl_2 \cdot 2THF$ dissolved immediately, leaving a slightly turbid solution. Stirring for 15 hr yielded a perfectly clear, homogeneous solution. Distillation of 150 ml of benzene into the reaction mixture left it unchanged. Removal of solvent at reduced pressure until the total volume was approximately 20 ml caused the appearance of a precipitate which upon isolation was identified as LiCl. The filtrate precipitated more LiCl on standing. Removal of the remainder of the solvent yielded a gummy solid which solidified after prolonged pumping at 0.5 mm pressure. The infrared spectrum of this solid showed absorption bands at 1877 (m), 1802 (s), 1781 (s), 1618 (m, vb), 1238 (w), 1170 (w), 1115 (w), 1060 (m), 1028 (s), 967 (s), 916 (w), 875 (w), 754 (m), 657 (m), 580 (w), and 460 (m) cm^{-1}. The X-ray powder pattern indicated the presence of LiCl plus many additional lines which do not match $BeCl_2 \cdot 2THF$. Addition of 60 ml of dry benzene to this solid produced a white slurry which was stirred for several hours and filtered. The white residue obtained had the following infrared spectrum: 1880 (w, b), 1830 (w, b), 1539 (s, b), 1189 (m, b), 1122 (w), 1062 (m), 998 (w), 972 (w), 898 (m), 803 (w), 724 (s), 563 (s), and 338 (w) cm^{-1}. The X-ray powder diffraction pattern indicated the presence of LiCl plus seven unidentified lines. *Anal.* Found for the solid: H, 1.26; Be, 0.764; Al, 13.4; Cl, 35.42. Removal of benzene from the filtrate yielded a gummy solid that did not solidify on prolonged pumping at reduced pressure with heating (65°, 24 hr). Slight discoloration of the material was noted along with some gas evolution, and the product was finally characterized as a plastic mass. *Anal.* Found for the product: H, 0.716; Be, 4.70; Al, 10.2; Cl, 16.1. The infrared spectrum of a Nujol mull of this product before heating at reduced pressure showed absorption bands at 1876 (s), 1810 (s), 1780 (sh), 1312 (w), 1267 (w), 1240 (w), 1169 (m), 1153 (w), 1116 (m), 1060 (s), 1028 (s), 965 (w), 948 (w), 901 (w), 843 (w), 760 (w, b), 722 (w, b), 664 (w), 570 (w, sh), and 463 (s) cm^{-1}. The infrared spectrum of a Nujol mull of the same sample after heating under vacuum showed absorption bands at 1876 (s, b), 1803 (s, sh), 1348 (w), 1266 (w), 1258 (m), 1238 (m), 1166 (s), 1114 (m), 1056 (s), 1023 (s, b), 959 (s, b), 898 (m), 826 (s, b), 642 (s, b), 573 (m, sh), 525 (m), and 458 (s) cm^{-1}.

The reaction was repeated in tetrahydrofuran at 0° using 8.46 mmol of $BeCl_2$ and 16.9 mmol of $LiAlH_4$ in 120 ml of tetrahydrofuran. The mixture was stirred for 15 hr at 0° yielding a slightly turbid solution. Removal of solvent at reduced pressure caused no solid precipitation until approximately 50% of the solvent had been removed. The final product of solvent removal was a gummy solid. Thirty-nine hours of pumping at reduced pressure (0.1 mm, 25°) yielded a plastic solid whose infrared spectrum showed absorption bands at 1778 (vs, b), 1575 (sh), 1237 (m), 1170 (s), 1110 (w), 1005

s), 960 (m), 920 (s), and 840 (s, b) cm^{-1}. Continued pumping (24 r) finally yielded a white powder whose infrared spectrum as a Nujol null showed absorption bands at 1802 (s, b), 1619 (s, b), and 457 w) cm^{-1}, plus an irregular base line which showed no definite absorption bands. The powder diffraction pattern of this solid indicated he presence of LiCl plus 11 additional lines which do not match $BeCl_2 \cdot 2THF$.

Reaction of $NaAlH_4$ and $BeCl_2$ in 1:1 Ratio in THF. To a stirred uspension of 15.6 mmol of $BeCl_2 \cdot 2THF$ in 150 ml of THF at 0° was dded 15.6 mmol of $NaAlH_4$. A white precipitate formed and the eaction mixture was stirred for an additional 30 min prior to filtraion. Filtration produced a white solid residue and a clear filtrate. Removal of solvent from the filtrate by reduced pressure distillation, n the cold, gave a white solid. *Anal.* Found for the insoluble prodct: H, 0.806; Be, 2.94; Al, 1.28; Cl, 43.4. The infrared spectrum of a Nujol mull of the solid showed absorption bands at 1729 (s, b), 1350 (m, vb), 1011 (s), 955 (w), 912 (w), 863 (s), 730 (m, b), and 542 (m, b) cm^{-1}. The X-ray powder diffraction pattern showed the presence of $BeCl_2 \cdot 2THF$ and NaCl with three unidentified weak lines. *Anal.* Found for the solid isolated from the soluble portion of the reaction mixture: H, 2.72; Be, 4.08; Al, 21.2; Cl, 15.8. The infrared spectrum of a Nujol mull of this solid showed absorption bands at 1874 (s, b), 1573 (s, vb), 1160 (m, b), 1019 (s, b), 950 (s, b), 829 (s, b), 712 (s, b), 649 (s, b), 452 (m, b), 369 (w), and 343 (w) cm^{-1}. The X-ray powder diffraction pattern of this solid shows numerous lines, however it does not confirm the presence of $BeCl_2 \cdot 2THF$ or NaCl.

Reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 Ratio in Ether. $LiAlH_4$ (25.03 mmol) was added dropwise to 25.03 mmol of $BeCl_2$ in 250 ml of ether at 0° producing a white precipitate. Filtration yielded a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a clear glass puddle which disintegrated upon further evacuation to a powder having a crystalline appearance. *Anal.* Found for the insoluble material: H, 2.46; Be, 8.37; Al, 3.25; Cl, 62.2. The powder diffraction pattern showed LiCl plus three additional weak lines. The infrared spectrum of a Nujol mull of this solid had the following absorptions: 1758 (s, vb), 1350 (m, vb), 1022 (w), and 778 (m, vb) cm^{-1}. *Anal.* Found for the soluble product: H, 255; Be, 3.58; Al, 23.0; Cl, 26.1. The infrared spectrum of a Nujol mull of this product exhibits absorptions at 2200–1200 (s, b), 1190 (w), 1150 (w), 1091 (w), 1023 (w), 973 (w), 890 (w), 844 (w), 760 (w), 600 (w, b), and 444 (w) cm^{-1}. The X-ray powder pattern consisted of four diffused lines which match those found for the soluble species in the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio.

The reaction was repeated at −78° using 22.7 mmol of $BeCl_2 \cdot 2Et_2O$ and 22.7 mmol of $LiAlH_4$ in 200 ml of diethyl ether. Again a precipitate formed immediately. After stirring for 45 min, filtration in the cold produced a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a white solid. *Anal.* Found for the insoluble residue: H, 2.08; Be, 9.02; Al, 3.46; Cl, 58.1. The infrared spectrum of a Nujol mull of the insoluble solid had the following absorptions: 1765 (s, vb), 1350 (m, vb), 1190 (w), 1150 (w), 1085 (w), 1017 (m), 890 (w), 883 (m), and 841 (w) cm^{-1}. The X-ray powder pattern showed the LiCl pattern plus one weak, unidentified line. *Anal.* Found for the solid isolated from the soluble portion of this reaction mixture: H, 3.25; Be, 1.08; Al, 28.2; Cl, 34.0. The infrared spectrum of a Nujol mull of this solid exhibited absorptions at 1851 (m, vb), 1615 (m, vb), 1257 (w), 1187 (w), 1145 (w), 1086 (w), 1014 (w), 968 (w), 888 (w), 730 (m, b), 620 (w), and 443 (w) cm^{-1}. The X-ray powder diffraction pattern contained four weak lines.

The above reaction was repeated at room temperature in order to compare the results obtained at the lower temperature. To 100 ml of $BeCl_2$ in diethyl ether (0.2325 *M*) was added 19.5 ml of $LiAlH_4$ in ether (1.119 *M*). The solution was stirred overnight and then filtered producing a white solid and a clear solution. Analysis of the solid gave an Al:Be:H:Cl ratio of 0.0:1.00:2.18:1.85. The solid contained 52% of the original beryllium. Analysis of the solution gave an Al:Be:H:Cl ratio of 1.0:0.44:2.99:1.07. The infrared spectrum of the solution showed bands at 1840, 1795, 972, 908, 772, and 725 cm^{-1}.

Reaction of BeH_2 and AlH_3 in 1:2 Ratio in THF and Diethyl Ether. To 7.6 mmol of BeH_2 was added 15.0 mmol of AlH_3 in THF. The solution was stirred 2 days and then filtered. Analysis of the filtrate showed no beryllium in solution. The infrared spectrum of the solution corresponded to AlH_3 and the intensity had not changed. Similar results were obtained in diethyl ether.

Infrared Spectra of Reaction Solutions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether. Molar increments of $LiAlH_4$ in ether were added to 9.23 mmol of $BeCl_2$ dissolved in 50 ml of diethyl ether. After the hydride addition, the mixture was stirred for 30 min to 1 hr, the precipitate was allowed to settle, and samples (1 ml) of the clear supernatant were withdrawn by syringe for infrared examination. Absorptions at a 1:1 hydride:halide ratio were (solvent bands omitted) 1348 (s), 1787 (s), 1638 (w), 964 (m), 904 (m), 764 (s), 712 (s), 569 (w), and 502 (w) cm^{-1}. These bands were unchanged on stirring for 16 hr. Absorptions at a 2:1 ratio were 1811 (s, sh), 1787 (s), 1638 (w), 900 (w), 753 (s), 675 (m), and 540 (w) cm^{-1}. Absorptions at a 3:1 ratio were 1812 (s, sh), 1785 (s), 1747 (s), 900 (w), 754 (s), 685 (m), and 540 (w) cm^{-1}. Filtration of the mixture produced a white residue which had the following spectrum after drying at reduced pressure: 1754 (s, b), 1350 (m, b), 1025 (w), and 752 (s, b) cm^{-1}. The powder diffraction pattern of this solid showed only LiCl and a single additional, indistinct line. Removal of ether from the clear, colorless filtrate produced a white solid having the following infrared spectrum: 1778 (s, b), 1618 (s, b), 1147 (w), 1026 (s), 891 (m, sh), 802 (w, sh), 720 (s, b), and 600 (s) cm^{-1}. The X-ray powder diffraction pattern of this solid contained eight lines. A sample of $LiAlH_4$ solution was stripped of solvent at 25° to yield a white solid whose infrared spectrum was 1778 (s, b), 1666 (s, b), 1148 (w), 867 (s, b), and 714 (s, b) cm^{-1}. The X-ray powder pattern of this partially desolvated hydride did not match the pattern for the ether-soluble product described above. The soluble reaction product was unstable and decomposed to a dark gray solid with gas evolution.

Infrared Spectra of Reaction Solutions of $LiAlH_4$ and $BeCl_2$ in THF. $LiAlH_4$ in THF was added to 4.54 mmol of $BeCl_2$ in 50 ml of tetrahydrofuran. Spectra were recorded for samples of the clear, homogeneous solution. Absorptions at 0:1 ratio: 665 (s, sh), 574 (m), and 524 (w) cm^{-1}. Absorptions at 1:1 ratio: 1730 (s, b), 773 (m), 729 (m), 670 (s, sh), and 378 (w) cm^{-1}. Absorptions at 2:1 ratio: 1730 (s, sh), 1701 (s), 776 (s), 731 (w), 680 (m, sh), and 370 (m, b) cm^{-1}. Absorptions at 3:1 ratio: 1730 (s, sh), 1695 (s), 1646 (m, sh), 774 (s), 731 (w), 680 (m, sh), and 370 (m, b) cm^{-1}. Absorptions at 7:1 ratio: 1691 (s), 1646 (s, sh), 763 (s), 733 (m, sh), 679 (m), 530 (w), and 384 (s) cm^{-1}. Absorptions of $LiAlH_4$ solution: 1691 (s), 763 (s), and 390 (m) cm^{-1}.

Infrared Spectra of Reaction Solutions of $NaAlH_4$ and $BeCl_2$ in THF. The procedure was the same as above except that the precipitate formed would not settle on standing for 1 hr. At a 2:1 ratio, the mixture was filtered and the infrared spectrum of the filtrate examined. Absorptions were found at 1736 (s), 1269 (w, sh), 797 (w), and 724 (m) cm^{-1}. $NaAlH_4$ in THF has absorptions at 1680 and 772 cm^{-1}.

Results and Discussion

The reaction of complex aluminum hydrides, $MAlH_4$ (where M = Li, Na, K), and metal halides of group II, $M'X_2$ (where M' = Be, Mg, Zn, Cd, Hg), can be visualized in either of two ways, depending on whether one considers the structure of an alkali metal aluminum hydride to be best represented by $M^{\delta+} \cdots (AlH_4)^{\delta-}$ or $M^{\delta+} \cdots H^{\delta-}-AlH_3$. If the alkali metal aluminum hydride is represented as an undissociated ion pair ($M^{\delta+} \cdots (AlH_4)^{\delta-}$), then the reaction can be represented as a simple metathetical exchange reaction in which the dipoles of polar bonds align in the appropriate way for exchange to take place

$$MAlH_4 + M'X_2 \longrightarrow \left[M^{\delta+}-(AlH_4)^{\delta-} \;\; X^{\delta-}-M'^{\delta+}-X \right] \longrightarrow XM'AlH_4 + MX \qquad (6)$$

$$XM'AlH_4 + MAlH_4 \longrightarrow \left[M^{\delta+}-(AlH_4)^{\delta-} \;\; X^{\delta-}-M'^{\delta+}-AlH_4 \right] \longrightarrow$$

$$M'(AlH_4)_2 + MX \qquad (7)$$

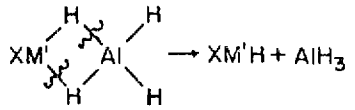
When M = Li or Na, M' = Mg, and X = Cl, Br, or I, the above reactions are observed.[5] Reaction 6 is observed when the ratio of $MAlH_4$ to MgX_2 is 1:1 and reaction 7 is observed when 1 additional mol of $MAlH_4$ is added (when M = Na). When M' is a less electropositive metal than aluminum, com-

pounds such as $XM'AlH_4$ and $M'(AlH_4)_2$ are not stable. Hence, although the reaction may proceed through pathways 6 and 7, disproportionation of these compounds to more stable products takes place

$$XM'AlH_4 \rightarrow XM'H + AlH_3 \quad (8)$$

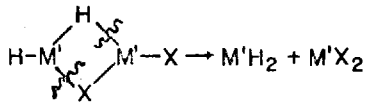
$$M'(AlH_4)_2 \rightarrow M'H_2 + 2AlH_3 \quad (9)$$

The disproportionation of $XM'AlH_4$ could be represented by a simple dissociation of metal-hydrogen bridge bonds



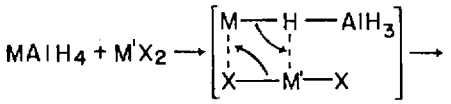
$$\rightarrow XM'H + AlH_3 \quad (10)$$

The compound XM'H is not stable when M' = Mg and has been shown to disproportionate further to $M'H_2$ and $M'X_2$.[12]

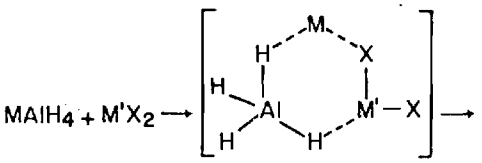


$$\rightarrow M'H_2 + M'X_2 \quad (11)$$

As stated earlier, another possible reaction pathway involves the visualization of a complex metal hydride as a hydrogen-bridged species reacting through either a four- or a six-center transition state (eq 12 and 13). Of course, XM'H-



$$\rightarrow MX + XM'H\text{–}AlH_3 \quad (12)$$



$$\rightarrow MX + XM'H\text{–}AlH_3 \quad (13)$$

AlH_3 ($XM'AlH_4$) can disproportionate by hydrogen bridge dissociation to XM'H and AlH_3. It is not necessary that MX and HM'X be separate species; thus it should be possible to isolate $MX \cdot M'HX$ (or $MM'X_2H$) as a single compound depending on the nature of M and M'. Furthermore, reaction of $MX \cdot M'XH$ with another molecule of $MAlH_4$ could result in the substitution of H for X with the resultant formation of $M'H_2$ (eq 14). Which of these pathways is actually taking

$$MX \cdot M'XH + MAlH_4 \rightarrow 2MX + M'H_2 + AlH_3 \quad (14)$$

place and to what extent should depend on the nature of M, M', and X. Although pathways 6 and 7 describe the reaction of $NaAlH_4$ with MgX_2, it appears that the pathways described by eq 8–14 are in operation when the electropositivity of M' is less than or equal to that of aluminum as in the case of beryllium.

The approach taken to study the reactions of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in diethyl ether and THF was to mix solutions of the $MAlH_4$ and BeX_2 compounds in 1:1 and 2:1 ratios and carry out complete elemental analysis on the resulting solution and on any precipitate that formed. In addition all precipitates were subjected to dta-tga, powder diffraction, and infrared analysis, and all solutions were further investigated by infrared spectroscopy. Because infrared analysis is so important in these studies, the reader might find the following generalizations useful in the interpretation of the data that follows. Terminal Al-H stretching frequencies occur between 1912 and 1660 cm^{-1} and may be lower in bridging situations (1550 cm^{-1}). Deformation modes of AlH_4^- are observed at *ca.* 750 cm^{-1}. Shifts in Al-H stretching frequencies have been correlated with the increase or decrease of the coordination number of aluminum. In general, increasing the coordination number of aluminum will cause the Al-H stretching frequency to decrease.[13] We[14] have discussed the shift in the Al-H stretching frequency in terms of covalent interactions for selected derivatives of complex aluminum hydrides.

Reactions in Diethyl Ether. Since $NaAlH_4$ is not soluble in ether, $LiAlH_4$ was the only hydride studied in this solvent involving the reactions of $MAlH_4$ compounds with beryllium chloride. The results of reactions of $LiAlH_4$ with $BeCl_2$ in ether at 1:1 and 2:1 ratios at +25 and −78° are recorded in Tables I and II.

$LiAlH_4$ and $BeCl_2$ in 2:1 Ratio. The reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio is rapid and complete within 1 hr even at −78°. At this stoichiometric ratio aluminum hydride is recovered virtually uncontaminated, except by residual solvent, from the soluble portion of the reaction mixture. The infrared spectrum of the reaction solution has a strong absorption at 1787 cm^{-1}, which does not agree closely with the value of 1801 cm^{-1} observed by Ehrlich[15] for a metastable solution of AlH_3 prepared from $LiAlH_4$ and $AlCl_3$ using the method of Finholt.[16] Aluminum hydride prepared in diethyl ether by this latter reaction precipitates from solution within minutes after its separation from the LiCl by-product. In contrast, the AlH_3 generated by $LiAlH_4$-$BeCl_2$ interaction is stable in ether solution over a period of at least 135 hr at room temperature. A slight precipitate does appear after 24 hr. However, the AlH_3 concentration drops only 4% after 1 week. The dta-tga for $AlH_3 \cdot 0.25OEt_2$ shown in Figure 2 indicates that the AlH_3 begins to lose ether at about 50°. Hydrogen evolution begins at 90° and is centered at 110°.

The ether-insoluble product of this reaction gave an analysis which indicated the product to be a mixture of LiCl and BeH_2 in 2:1 ratio. However, when the reaction mixture is worked up rapidly, the X-ray powder pattern data (Table III) indicate that the product is not a physical mixture of LiCl and BeH_2. The only other possibility appears to be that it is a complex as shown in eq 15. When this solid was stirred

$$2LiAlH_4 + BeCl_2 \rightarrow Li_2BeCl_2H_2 + 2AlH_3 \quad (15)$$

in ether for several days, the X-ray powder pattern of the product was consistent with a physical mixture of LiCl and BeH_2. The dta curve for the complex ($Li_2BeCl_2H_2$) (Figure 1) shows that it decomposes endothermally at 160°, whereas the same product, stirred for 3 days in ether, shows an exothermal decomposition at 185° (Figure 3). Further evidence supporting complex formation rests on the fact that BeH_2 is insoluble in THF, yet a mixture of BeH_2 + 2 LiCl dissolves in THF after stirring overnight. The infrared spectrum of the resulting solution shows bands at 1825, 1650, and 775 cm^{-1}.

Thus, neither the original report of the preparation of $Be(AlH_4)_2$ by Wiberg[1] or the later report by Wood and Brenner[2] could be substantiated although the report by

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Table I. Reactions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether at 25°

$LiAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
1:1	Sol	3.08:1.0	1.0:5.22	1.0:1.85
1:1	Insol	20.2:1.0	2.24:1.0	1.0:1.89
2:1	Sol	3.12:1.0	No Be	No Be
2:1	Insol	11.0:1.0	2.22:1.0	1.0:2.0

Table II. Reactions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether at −78°

$LiAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
1:1	Sol	3.09:1.0	1.0:2.22	1.0:2.84
1:1	Insol	16.2:1.0	1.69:1.0	1.0:1.64
2:1	Sol	3.18:1.0	No Be	No Be
2:1	Insol	10.5:1.0	2.06:1.0	1.0:2.05

Table III. X-Ray Powder Diffraction Data for $Li_2BeCl_2H_2$[a]

1		2		3		4	
d, Å	I[b]	d, Å	I	d, Å	I	d, Å	I
3.96	s	3.96	w	3.30	w	2.967	100
3.42	w			2.96	s		
2.98	w	2.95	s	2.85	vvw		
2.70	vs	2.70	s	2.70	vw		
2.56	w	2.56	s	2.56	s	2.57	85
2.42	w						
2.30	vw						
2.21	m	2.20	vw				
2.11	vw						
2.04	vw			2.00	vw		
1.93	s						
1.90	s	1.91	w				
1.86	w						
1.71	w	1.80	m				
1.615	w			1.81	s	1.817	58
1.64	vw						

[a] Species: 1, precipitate of 2 $LiAlH_4$ + $BeCl_2$ obtained immediately after mixing; 2, precipitate of 2 $LiAlH_4$ + $BeCl_2$ obtained 2 hr after mixing; 3, product 1 stirred 3 days in Et_2O; 4, LiCl (ASTM). [b] Key: w, weak; m, medium; s, strong; v, very.

Holley and Lemons[3] was found to be substantially correct. Also, no evidence was found for the formation of $LiBe(AlH_4)_3$ in reactions between $LiAlH_4$ and $BeCl_2$ in diethyl ether, under the conditions reported herein.[4]

Contrary to reports by Dymova,[9] $LiAl_2H_7$ is not the product in solution upon reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio (eq 16). We have prepared HBeCl by an independent

$$2LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \quad (16)$$

method and have found that it is soluble in ether. We have found less than 0.8% lithium in the soluble products of the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether and an Al:Li ratio of approximately 17. X-Ray powder diffraction data for these soluble products do not match those of the Russian report. The powder pattern of $AlH_3 \cdot 0.25OEt_2$ which we have isolated from the 2:1 reaction at 25° does agree well with the powder pattern of $AlH_3 \cdot 0.25OEt_2$ reported by French workers.[17]

$LiAlH_4$ and $BeCl_2$ in 1:1 Ratio. For the reactions where the $LiAlH_4$:$BeCl_2$ ratio is 1:1, the reaction is more complex. Infrared data, elemental analysis, and X-ray powder diffraction data of the insoluble reaction product show that the major constituents are LiCl and BeH_2. Elemental analysis of the soluble portion of the reaction indicates empirically a mixture of 2 AlH_3 and $BeCl_2$. However, studies of the reaction of AlH_3 and $BeCl_2$ in ether[18] show that redistribution between AlH_3 and $BeCl_2$ takes place according to eq 17 and

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \quad (17)$$

18. Thus, the reaction of $LiAlH_4$ and $BeCl_2$ in ether in 1:1

$$2AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl + AlH_3 \quad (18)$$

ratio can be represented by eq 19.

$$2LiAlH_4 + 2BeCl_2 \rightarrow 2LiCl\downarrow + BeH_2\downarrow + HBeCl + AlH_2Cl + AlH_3 \quad (19)$$

Reactions in Tetrahydrofuran. Both $NaAlH_4$ and $LiAlH_4$ were allowed to react with $BeCl_2$ in THF. Of the alkali metal halide by-products, NaCl is insoluble while LiCl is soluble in THF. Because of the solubility of LiCl in THF the reaction course is more complicated when $LiAlH_4$ is involved since LiCl can then interact with other products in solution such as AlH_3 and BeH_2. However, NaCl eliminates the above possibilities and hence the reaction course is not as complicated. A summary of results of reactions of $NaAlH_4$ with $BeCl_2$ in 1:1 and 2:1 ratio at 25 and 0° are recorded in Tables IV and V.

$NaAlH_4$ and $BeCl_2$ in 2:1 Ratio. When $NaAlH_4$ was allowed to react with $BeCl_2$ in a 2:1 ratio in THF, the results were found to be very similar to the results obtained for the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. The soluble reaction product is AlH_3 which was identified by elemental and infrared analyses (strong absorption at 1800 and 1625 cm^{-1} (Nujol)). The insoluble reaction products are NaCl and BeH_2 (the terminal Be–H stretching frequency occurs at 1710 cm^{-1} when the product is isolated from THF). X-Ray powder diffraction studies on the solid product show it to be a physical mixture of BeH_2 and NaCl and not a complex as had been observed in the case of LiCl and BeH_2 (*i.e.*, $Li_2BeH_2Cl_2$).

$$2NaAlH_4 + BeCl_2 \rightarrow 2AlH_3 + 2NaCl\downarrow + BeH_2\downarrow \quad (20)$$

$NaAlH_4$ and $BeCl_2$ in 1:1 Ratio. The reaction of $NaAlH_4$ and $BeCl_2$ in 1:1 ratio in THF is more complex than the same reaction carried out in 2:1 mole ratio. The insoluble product mixture was shown by elemental analysis and X-ray powder diffraction data to contain NaCl, BeH_2, and a small amount of $BeCl_2 \cdot 2THF$ as the principal components. Analytical data suggest that the soluble species are AlH_3, H_2AlCl, and HBeCl. Although HBeCl has only limited solubility in THF, the addition of AlH_3 to a slurry of HBeCl in THF causes all the HBeCl to dissolve. The solution spectrum of this mixture is unchanged from that of AlH_3; however, due to the increased solubility of HBeCl, it is concluded that a weak interaction to produce a compound of empirical formula $ClBeAlH_4$ is possible

$$AlH_3 + HBeCl \rightleftharpoons ClBeAlH_4 \quad (21)$$

Thus, the products of this reaction in 1:1 ratio (NaCl, BeH_2, and AlH_3) are the same as the products produced when the ratio is 2:1 except that the AlH_3 formed reacts further with the additional amount of $BeCl_2$ present in 1:1 ratio. Thus, one could look at the reaction sequence in the following way

$$2NaAlH_4 + BeCl_2 \rightarrow 2NaCl + BeH_2 + 2AlH_3 \quad (22)$$

$$2AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl + AlH_3 \quad (23)$$

$$2NaAlH_4 + 2BeCl_2 \rightarrow 2NaCl\downarrow + BeH_2\downarrow + H_2AlCl + HBeCl + AlH_3$$

(17) J. Bousquet, J. Choury, and P. Claudy, *Bull. Soc. Chim. Fr.*, 3848 (1967).

(18) E. C. Ashby, P. Claudy, and R. Schwartz, *Inorg. Chem.*, in press.

Table IV. Reactions of $NaAlH_4$ and $BeCl_2$ in THF at 0°

$NaAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
1:1	Sol	3.47:1.0	1.0:1.23	1.02:1.0
1:1	Insol	16.9:1.0	1.0:1.23	1.0:1.52
2:1	Sol	3.14:1.0	1.0:1.23	8.40:1.0
2:1	Insol	19.2:1.0	1.84:1.0	1.0:2.13

Table V. Reactions of $NaAlH_4$ and $BeCl_2$ in THF at 25°

$NaAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
2:1	Sol	3.57:1.0	1.32:1.0	5.62:1.0
2:1	Insol	9.37:1.0	1.46:1.0	1.0:4.05

As mentioned earlier, we have studied the reaction of AlH_3 and $BeCl_2$ in diethyl ether[18] and have found that the reaction proceeds as shown in eq 23.

$LiAlH_4$ and $BeCl_2$. As was mentioned earlier, LiCl, the alkali metal halide by-product of the reaction of $LiAlH_4$ and $BeCl_2$ in THF, is soluble in THF. Since this is the only case studied where the alkali metal halide by-product is soluble in the reaction solvent, it is interesting to observe the effect that this solubility has on the reaction products. In order to simplify the interpretation of the results of the reaction between $LiAlH_4$ and $BeCl_2$, we shall consider first the independent interaction of the probable products of this reaction, *i.e.*, LiCl, BeH_2, AlH_3, and HBeCl.

When LiCl was added to a solution of AlH_3 in THF, complex formation was indicated by the change in the infrared spectrum of the solution. AlH_3 in THF absorbs at 1739 cm^{-1}; however, when LiCl is added, the infrared spectrum shows a band at 1705 cm^{-1} with a shoulder at 1745 cm^{-1}. This observation indicates an equilibrium of the type shown in eq 24. Earlier we observed the formation of this complex

$$LiCl + AlH_3 \rightleftharpoons LiAlH_3Cl \quad (24)$$

in diethyl ether.[19] Whereas LiCl is insoluble in ether, in the presence of an equimolar amount of AlH_3, it is soluble.

The complex $Li_2BeH_2Cl_2$ formed in ether was found to be soluble in THF and the infrared spectrum showed weak lines at 1825 and 1650 cm^{-1}. The fact that the complex $Li_2BeH_2Cl_2$ is soluble in THF and BeH_2 is insoluble indicates that the complex is stable in THF and therefore some interaction between LiCl and BeH_2 in THF takes place

$$2LiCl + BeH_2 \rightarrow Li_2BeH_2Cl_2 \quad (25)$$

It was also found that when a THF solution of LiCl was added to preformed BeH_2 and stirred overnight, 20% of the beryllium was found in solution.

When $LiAlH_4$ was allowed to react with HBeCl in THF, the resulting clear solution showed ir bands at 1730 (sh), 1700, 775, and 740 cm^{-1}. If the shoulder at 1730 cm^{-1} is assigned to AlH_3, then the band at 1700 cm^{-1} could be assigned to a terminal Be–H stretching vibration in $LiBeH_2Cl$ (eq 26).

$$LiAlH_4 + HBeCl \xrightleftharpoons{THF} LiBeH_2Cl + AlH_3 \quad (26)$$

This band could not be assigned to $LiAlH_3Cl$ since, if this were formed, then BeH_2 would also be formed and would precipitate from solution (eq 27).

$$LiAlH_4 + HBeCl \not\rightarrow LiAlH_3Cl + BeH_2 \quad (27)$$

Interactions between Be–H and Al–H compounds appear to be very weak or nonexistent. In the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether no evidence for $Be(AlH_4)_2$ was found. No reaction was observed between BeH_2 and AlH_3 in diethyl ether or in THF. Beryllium was found in solution only in cases where cleavage of the THF solvent had occurred. As was pointed out earlier, when AlH_3 was allowed to react

$$BeH_2 + 2AlH_3 \xrightarrow[\text{or } Et_2O]{THF} Be(AlH_4)_2 \quad (28)$$

with HBeCl in THF, the spectrum corresponded to that of a solution of AlH_3 in THF.

$LiAlH_4$ and $BeCl_2$ in 2:1 Ratio. When $LiAlH_4$ was allowed to react with $BeCl_2$ in 2:1 ratio in THF, the ir spectrum of the solution exhibited bands at 1730 (sh) and 1701 cm^{-1}. This is similar to the spectrum obtained from the mixture of LiCl and AlH_3 which is attributed to $LiAlH_3Cl$. It is also similar to that obtained from the reaction of $LiAlH_4$ and HBeCl in THF which is postulated to yield AlH_3 and $LiBeH_2Cl$. If the solvent is removed from the 2:1 mixture of $LiAlH_4$ and $BeCl_2$ and benzene is added, a solid is obtained which was identified as LiCl (40% of theoretical). Since the interaction of LiCl and AlH_3 is described by an equilibrium as indicated by the infrared spectrum of the mixture, the removal of solvent and addition of benzene could cause the removal of LiCl from this equilibrium. This would leave AlH_3 in solution and the beryllium could continue to be solubilized as $LiBeH_2Cl$. When all the solvent was removed from the reaction product and the resulting solid was extracted with benzene, 56% of the theoretical amount of AlH_3 was extracted into the benzene solution.

If the complex $Li_2BeH_2Cl_2$ is allowed to react with 2 mol of AlH_3 in THF, a clear solution results. The infrared spectrum of this solution is identical with the spectrum from the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio. This observation is best explained by the displacement of one of the LiCl molecules of the complex ($Li_2BeH_2Cl_2$) by AlH_3 to yield $LiAlH_3Cl$ and $LiBeH_2Cl$. The reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio and of $Li_2BeH_2Cl_2$ in admixture with 2 mol of AlH_3 can then be understood as an equilibrium mixture described by

$$2LiAlH_4 + BeCl_2 \rightarrow LiAlH_3Cl + LiBeH_2Cl + AlH_3 \rightleftharpoons Li_2BeH_2Cl_2 + 2AlH_3 \quad (29)$$

As $LiAlH_4$ was added to $BeCl_2$ in THF in ratios greater than 2:1, the only changes observed in the spectrum were due to the appearance of a band at 1691 cm^{-1} due to excess $LiAlH_4$.

When $LiAlH_4$ was allowed to react with $BeCl_2$ in a 1:1 ratio in THF, the ir spectrum of the solution exhibited a broad band centered at 1730 cm^{-1}. If one assumes that the products are identical with those observed in the 1:1 case in diethyl ether (eq 30), then one would expect bands at 1836 and

$$2LiAlH_4 + 2BeCl_2 \rightarrow HBeCl + AlH_2Cl + AlH_3 + Li_2BeCl_2H_2 \quad (30)$$

1755 cm^{-1} due to AlH_2Cl.[20] However, these bands are not observed in the 1:1 reaction of $LiAlH_4$ and $BeCl_2$ in THF; therefore, AlH_2Cl cannot be present in the reaction mixture. The products of this reaction can be satisfactorily explained if one assumes that the LiCl generated in the reaction complexes with other products of the reaction (*e.g.*, HBeCl) in a manner similar to the 2:1 case in THF which is discussed above. The reaction could therefore be described by eq 31.

$$LiAlH_4 + BeCl_2 \rightarrow LiCl + HBeCl + AlH_3 \rightarrow LiBeCl_2H + AlH_3 \quad (31)$$

(19) E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, 88, 729 (1966).

(20) D. L. Schmidt and E. E. Flagg, *Inorg. Chem.*, 6, 1262 (1967).

In a separate experiment LiCl in THF was added to HBeCl. The ir spectrum of the resulting clear solution showed a very weak broad band at 1700 cm^{-1}. At the same concentration AlH_3 in THF shows a very intense band at 1739 cm^{-1}. One might, therefore, expect that a 1:1 mixture of $LiBeCl_2H$ and AlH_3 would give an ir spectrum with a broad band centered at approximately 1730 cm^{-1} as we indeed found for the reaction product of $LiAlH_4$ and $BeCl_2$ in THF. The predicted spectra of other possible products are not consistent with the observed spectrum of the reaction product of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in THF. The only difference between the reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in ether and THF (eq 30 and 31) is the fact that in THF (eq 31) the AlH_3 formed does not react with HBeCl to form BeH_2 and H_2AlCl. This observation is not inconsistent with known reactivity differences of AlH_3 or other aluminum compounds in THF compared to ether.

Acknowledgment. The authors gratefully acknowledge support of this work by the Office of Naval Research Contract No. N--14-67-A-0159-0005.

Registry No. $BeCl_2 \cdot 2THF$, 15663-55-5; $BeCl_2 \cdot 2Et_2O$, 14267-69-7; $LiAlH_4$, 16853-85-3; $BeCl_2$, 7787-47-5; $NaAlH_4$, 13770-96-2; HBeCl, 42016-55-7; AlH_3, 7784-21-6; BeH_2, 7787-52-2; $Li_2BeCl_2H_2$, 39405-85-1; $AlH_3 \cdot 0.25OEt_2$, 2835-71-1.

[Reprinted from Inorganic Chemistry, 12, 2493 (1973).]

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A New and Convenient Method for the Preparation of Complex Metal Hydrides of Group II Metals. Synthesis of Complex Metal Hydrides of Zinc

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Received April 16, 1973

A series of complex metal hydrides of zinc with composition $M_nZn_mH_{2m+n}$, where M = Li, Na, or K, has been synthesized by reacting an appropriate "ate" complex of zinc ($M_nZn_mR_{2m+n}$) with either $LiAlH_4$, $NaAlH_4$, or AlH_3. The 1:1, 2:1, and 3:1 complexes of methyllithium and dimethylzinc yielded $LiZnH_3$, Li_2ZnH_4, and Li_3ZnH_5 when allowed to react with lithium aluminum hydride in diethyl ether. The reaction of potassium hydride with dimethylzinc in 1:1 and 1:2 ratios in tetrahydrofuran yielded potassium dimethylhydridozincate [$KZn(CH_3)_2H$] and potassium tetramethylhydridodizincate [$KZn_2(CH_3)_4H$]. KZn_2H_5 resulted when either $KZn(CH_3)_2H$ or $KZn_2(CH_3)_4H$ was allowed to react with AlH_3 in tetrahydrofuran; whereas, $KZnH_3$ was obtained from the reaction of $KZn(CH_3)_2H$ with lithium aluminum hydride in the same solvent. Both the 1:1 and 1:2 complexes of sodium hydride with dimethylzinc gave $NaZnH_3$ when allowed to react with sodium aluminum hydride in tetrahydrofuran. These reactions are presented as examples of a new and general route for the preparation of complex metal hydrides by the reaction of "ate" complexes with complex metal hydrides of aluminum or AlH_3.

Introduction

Complex metal hydrides of aluminum and boron (*e.g.*, $LiAlH_4$ and $NaBH_4$) have proven to be invaluable reagents in organic synthesis. These compounds are prepared by the reaction of a group IA metal hydride with a group IIIA metal derivative (eq 1 and 2).[1,2] Recently we reported the prep-

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl \quad (1)$$

$$4NaH + (CH_3O)_3B \rightarrow NaBH_4 + 3NaOCH_3 \quad (2)$$

aration of the first complex metal hydride of magnesium ($KMgH_3$) by the hydrogenolysis of an "ate" complex of magnesium (eq 3).[3] The necessity for this synthetic scheme

$$KH + (sec\text{-}C_4H_9)_2Mg \rightarrow KMg(sec\text{-}C_4H_9)_2H \xrightarrow{H_2} KMgH_3 + 2C_4H_{10} \quad (3)$$

is due to the fact that the reaction of KH directly with $MgCl_2$ (analogous to the preparation of $LiAlH_4$) produces MgH_2 and not $KMgH_3$.[4] The particular R_2Mg compound used [$(sec\text{-}Bu)_2Mg$] is difficult to prepare but its use is necessitated by the fact that it is the only known R_2Mg compound soluble in benzene and benzene solvent is necessitated due to the fact that $MMgR_2H$ compounds (where M = Li, Na, or K) cleave ether solvents.[5,6] In addition, it is known that R-Mg compounds can be hydrogenolyzed to H-Mg compounds most easily when the R group is branched in the α position, such as in *sec*-butyl compounds.[7]

Analogous to the reaction of KH with $MgCl_2$, the reaction of KH with $ZnCl_2$, NaH with ZnI_2, or LiH with $ZnBr_2$ all yield ZnH_2 instead of complex metal hydrides of zinc. For this reason the synthesis of K_2ZnH_4 and Na_2ZnH_4,[8] reported recently, was carried out by reaction of an "ate" complex of zinc (eq 4). In view of this success we wished to

$$4KH + 3(sec\text{-}C_4H_9)_2Zn \rightarrow K_2ZnH_4 + 2KZn(sec\text{-}C_4H_9)_3 \quad (4)$$

expand our synthetic studies to include other complex metal hydrides of zinc. Our initial plan was to investigate the reaction of LiH with di-*sec*-butylzinc in both hydrocarbon and ether solvents in an attempt to prepare a spectrum of lithium dialkylzinc hydrides ranging from $Li_3ZnR_2H_3$ to $LiZn_3R_6H$, where R = *sec*-butyl. The lithium dialkylzinc hydrides were to be converted to the corresponding complex metal hydrides by high-pressure hydrogenation, since the carbon-zinc bond of the *sec*-butylzinc group should be easily converted to an H-Zn bond by hydrogenation (see eq 3).

Our initial plan proved to be unfeasible when the intermediate lithium *sec*-butylzinc hydrides were found to cleave ether solvents too rapidly for hydrogenation to be an effective tool for R-Zn to H-Zn conversion. Unfortunately, the above reaction did not take place at all in benzene. The plan was modified in two ways. First, conversion of R-Zn to H-Zn was carried out by reaction of the "ate" complex with $LiAlH_4$ since alkyl exchange from zinc to aluminum and hydrogen exchange from aluminum to zinc might be expected at temperatures lower than 0°. At these temperatures

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$MZnR_2H$ and $MZnR_3$ compounds should not cleave ether solvents. Second, dimethylzinc could be used as a starting material rather than di-*sec*-butylzinc since methyl group exchange should be more rapid than *sec*-butyl group exchange (eq 5 and 6). In addition, Shriver and coworkers,[9] in their

$$LiCH_3 + Zn(CH_3)_2 \rightarrow LiZn(CH_3)_3 \xrightarrow{LiAlH_4} LiZnH_3 + LiAl(CH_3)_3H \quad (5)$$

$$NaH + Zn(CH_3)_2 \rightarrow NaZn(CH_3)_2H \xrightarrow{NaAlH_4} NaZnH_3 + NaAl(CH_3)_2H_2 \quad (6)$$

report on the preparation and properties of $MZnR_2H$ compounds, showed that $LiZn(CH_3)_2H$ and $NaZn(CH_3)_2H$ are better defined species in solution than the higher alkyl analogs.

The advantages of using this method for preparation of complex metal hydrides of zinc are as follows: (1) the reactions are instantaneous and quantitative, (2) no ether cleavage products are formed, (3) high-pressure hydrogenation is not required, and (4) methyl-metal compounds in ether are much easier to prepare than the *sec*-butyl compounds in hydrocarbon solvent.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques. Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice–acetone to remove solvent vapors.[10]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as Nujol mulls between CsI plates. Solutions were run in matched 0.10-mm path length NaCl cells. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. A 300-ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high-pressure hydrogenation. Dta–tga data were obtained under vacuum with a modified Mettler thermoanalyzer II. A diagram of the vacuum line attached to the balance chamber is shown in Figure 1. Operation of the dta–tga under vacuum with the U trap between R_1 and the pump cooled to liquid nitrogen temperature permits one to distinguish between condensable and noncondensable evolved gases by use of the gauges J_1 and J_2. The U-shaped tube can also be used as an analytical device to separate the condensed gases after the desired temperature limit has been reached. After the liquid nitrogen has been removed, slow warming of the copper branch produces a vertical thermal gradient which assures a good separation of the trapped products, the more volatile ones escaping first. The vacuum line was constructed to allow the use of the dta–tga under various conditions: vacuum, static pressure, or gas flow. In the latter case, the gas enters the chamber by V and leaves through r_1 or r_2 and r_3; R_2 open, R_1 closed.[11]

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[10] Methane in the presence of hydrogen was determined by volume in a tensimeter. Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration. Halogens were determined by the Volhard procedure.

Materials. Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium at 4000 psig for 24 hr. Solutions of lithium and sodium aluminum hydride (Ventron, Metal Hydride Division) were prepared in both diethyl ether and tetrahydrofuran in the usual manner. Dimethyl- and di-*sec*-butylzinc were prepared by the procedure of Noller.[12] Methyl and *sec*-butyl iodides were obtained from Fisher Scientific Co. The iodides were dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc–copper couple was obtained from Alfa Inorganics. The reactions of zinc–copper couple with methyl iodide were allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture at atmospheric pressure under nitrogen while di-*sec*-butylzinc was distilled at reduced pressure. Methyllithium (made from CH_3Cl) was obtained as a 5% solution in ether from Matheson Coleman and Bell and stored at −20° until ready to use. Tetrahydrofuran and benzene (Fisher Certified Reagent Grade) were distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher Reagent) over lithium aluminum hydride. Ultrapure hydrogen (99.9995%) obtained from the Matheson Corp. was used for hydrogenation experiments. Alane was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration and a lithium-free solution of AlH_3 in THF was obtained.[13]

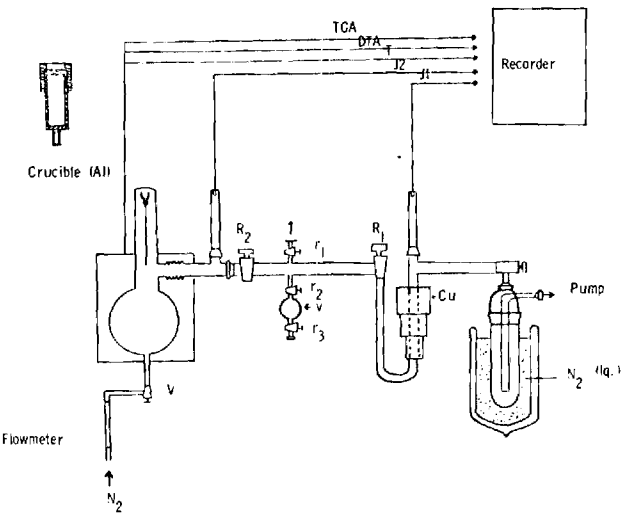

Figure 1. Description of high-vacuum portion of Mettler thermoanalyzer II.

Reactions Involving $(sec\text{-}C_4H_9)_2Zn$. (a) Reaction of LiH and $(sec\text{-}C_4H_9)_2Zn$ in Benzene. Di-*sec*-butylzinc (66 mmol) in benzene was added to a slurry of LiH (66 mmol) in benzene. The mixture was filtered after it had been stirred for 1 week. The filtrate showed a Zn:*sec*-butyl ratio of 1:1.98, but no lithium or hydridic hydrogen was found. Analysis of the solid showed a Li:Zn:H ratio of 10:1:7.

(b) Reaction of LiH and $(sec\text{-}C_4H_9)_2Zn$ in THF. Di-*sec*-butylzinc (27.9 mmol) in THF was added to 27.9 mmol of a LiH slurry in THF. The mixture was stirred at room temperature overnight. A clear solution resulted which exhibited a Li:Zn:*sec*-C_4H_9:H ratio of 1.00:0.96:1.88:0.32. Gas chromatography of the hydrolysate showed a large butanol peak due to extensive THF cleavage. A similar reaction was carried out in such a way that all of the THF was removed under vacuum immediately after the lithium hydride dissolved, but the lithium di-*sec*-butylhydridozincate complex decomposed to lithium hydride and di-*sec*-butylzinc under vacuum. Thus, it was not possible to remove all the THF and dissolve the residue in a noncleaving solvent, such as benzene.

(c) Reaction of LiH and $(sec\text{-}C_4H_9)_2Zn$ in Diethyl Ether. Di-*sec*-butylzinc (28 mmol) in diethyl ether was added to a slurry of 28 mmol of LiH in diethyl ether. The mixture was stirred for 1 week and filtered. The filtrate showed a Li:Zn ratio of 0.20:1.00. The solid exhibited a Li:Zn:H ratio of 1.00:0.06:0.97. The reaction was repeated under reflux conditions for 2 weeks. Still little reaction occurred.

(d) Reaction of $LiZn(sec\text{-}C_4H_9)_2H$ with $LiAlH_4$ in THF. Preparation of Li_2ZnH_4. LiH (5.49 mmol) slurry in THF was added to 5.49 mmol of di-*sec*-butylzinc in THF. This mixture was stirred until all the lithium hydride dissolved (about 21 hr), then 8.11 mmol of $LiAlH_4$ in THF was added rapidly. After 5 min a white solid began to appear, and after 30 min the mixture had a slightly gray, thick, milky appearance. The mixture was stirred overnight at room temperature. The solid, now having a gray appearance, was separated by filtration and dried at room temperature *in vacuo*. *Anal.* Calcd for

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Li_2ZnH_4: Li, 16.7; Zn, 78.5; H, 4.85. Found: Li, 16.3; Zn, 79.5; H, 4.11. The molar ratio of Li:Zn:H is 1.93:1.00:3.36. The filtrate contained 8.50 mmol of aluminum, 3.40 mmol of zinc, and 10.31 mmol of lithium. The amount of Li_2ZnH_4 recovered was 2.09 mmol of a theoretical 2.75 mmol. The X-ray powder diffraction data are given in Table I. The infrared spectrum of the solid product (Nujol mull) showed two strong broad bands at 400–1000 cm^{-1} centered at 650 cm^{-1} and 1200–1650 cm^{-1} centered at 1450 cm^{-1}. This spectrum was very similar to that found for K_2ZnH_4.[5]

Reactions Involving $(CH_3)_2Zn$ and LiH. (a) Reaction of $LiZn(CH_3)_2H$ with $LiAlH_4$ in THF. Attempted Preparation of $LiZnH_3$. Dimethylzinc (10 mmol) in THF was added to 10 mmol of LiH slurry in THF. After 5 hr of stirring the solution was clear. $LiAlH_4$ (10 mmol) in THF was added quickly. After 1 min the solution became faintly cloudy, and after 30 min a thick white mixture was present. The mixture was stirred overnight at room temperature and filtered the next day. The precipitate, which had now become very gray due to decomposition to zinc metal, was dried at room temperature *in vacuo*. *Anal.* Calcd for $LiZnH_3$: Li, 9.2; Zn, 86.8; H, 4.0. Found: Li, 9.4; Zn, 87.2; H, 3.35. The molar ratio of Li:Zn:H was 1.00:1.00:2.51. The filtrate contained 10.78 mmol of aluminum, 1.41 mmol of zinc, and 11.20 mmol of lithium. The amount of solid recovered was 8.59 mmol of a theoretical 10 mmol. The X-ray powder diffraction data which are given in Table I showed lines for Li_2ZnH_4 and zinc metal only.

(b) Reaction of LiH and $(CH_3)_2Zn$ in 2:1 Ratio in THF. Attempted Preparation of $Li_2Zn(CH_3)_2H_2$. Lithium hydride slurry (20 mmol) in THF was added to 10 mmol of dimethylzinc in THF. The resulting mixture was stirred for 2 weeks at room temperature. A solid was always present. The solid was separated by filtration and dried at room temperature *in vacuo*. The solid had a molar ratio of Li:Zn of 15.22:1.00. The X-ray powder diffraction pattern of the solid product contained lines due to lithium hydride and zinc metal only. The Li:Zn ratio of the filtrate was 1.28:1.00.

(c) Reaction of $LiZn_2(CH_3)_4H$ with $LiAlH_4$ in THF. Attempted Preparation of $LiZn_2H_5$. Lithium hydride slurry (5 mmol) in THF was added to 10 mmol of dimethylzinc in THF. Within 5 min a clear solution resulted. After addition of 20 mmol of $LiAlH_4$ an infrared spectrum of the solution showed only bands due to $LiAlH_4$. After 30 min some gray solids began to appear. The mixture was stirred overnight at room temperature. The next day, very gray, almost black solids were present. The precipitate was separated by filtration and dried at room temperature *in vacuo*. The molar ratio of Li:Zn:H in the solid was 1.00:2.06:2.96. The filtrate contained 20.20 mmol of aluminum, 1.02 mmol of zinc, and 19.60 mmol of lithium. The gas evolved on hydrolysis of the filtrate was found to contain hydrogen to methane in the molar ratio 4.28:1.00. The infrared spectrum of the filtrate corresponded to a mixture of $LiAl(CH_3)_2H_2$ and $LiAlH_4$. X-Ray powder diffraction data for the solid which are given in Table I showed lines for Li_2ZnH_4 and zinc metal only. Infrared analysis (Nujol mull) of the solid showed three broad bands (400–700, 950–1150, and 1350–2000 cm^{-1}).

Reactions Involving $(CH_3)_2Zn$ with CH_3Li. (a) Reaction of $LiAlH_4$ with $LiZn(CH_3)_3$ in Diethyl Ether. Preparation of $LiZnH_3$. Methyllithium (5 mmol) in diethyl ether were added to 5 mmol of dimethylzinc in diethyl ether. The resulting solution was stirred at room temperature for 1 hr; then 7.5 mmol of $LiAlH_4$ in diethyl ether was added. A white precipitate appeared immediately. This mixture was stirred at room temperature for another hour and filtered. The white solid was dried at room temperature *in vacuo* and analyzed. *Anal.* Calcd for $LiZnH_3$: Li, 9.2; Zn, 86.8; H, 4.0. Found: Li, 9.2; Zn, 86.5; H, 4.30. The molar ratio of Li:Zn:H was 1.00:1.00:3.21. The filtrate contained 7.53 mmol of aluminum, no zinc, and 7.34 mmol of lithium. The amount of $LiZnH_3$ recovered was 5 mmol of a theoretical 5 mmol. The X-ray powder diffraction data are given in Table I.

(b) Reaction of $LiAlH_4$ with $Li_2Zn(CH_3)_4$ in Diethyl Ether. Preparation of Li_2ZnH_4. Dimethylzinc (10 mmol) in diethyl ether was added to 20 mmol of methyllithium in diethyl ether. The resulting solution was stirred for 1 hour at room temperature, followed by addition of 20 mmol of $LiAlH_4$ in diethyl ether. White solids appeared immediately; however, the mixture was stirred for an additional 1 hr at room temperature, filtered, and dried *in vacuo*. *Anal.* Calcd for Li_2ZnH_4: Li, 16.7; Zn, 78.5; H, 4.85. Found: Li, 14.8; Zn, 80.4; H, 4.85. The molar ratio of Li:Zn:H was 1.73:1.00:3.94. The filtrate contained 19.30 mmol of aluminum, no zinc, and 20.01 mmol of lithium. The amount of Li_2ZnH_4 recovered was 10 mmol of a theoretical 10 mmol. The X-ray powder diffraction data are given in Table I. Infrared analysis (Nujol mull) showed three broad bands [illegible] and 1400–1900 cm^{-1} (centered at 1580 cm^{-1})]. Infrared analysis of the filtrate (KBr cell, 0.10-mm path length) showed a strong peak in the Al–H stretching region centered at 1700 cm^{-1} and a moderate peak in the Al–H deformation region centered at 760 cm^{-1}. This spectrum is characteristic of the species $LiAl(CH_3)_2H_2$.

(c) Reaction of $LiAlH_4$ with $Li_3Zn(CH_3)_5$ in Diethyl Ether. Preparation of Li_3ZnH_5. Methyllithium (15 mmol) in diethyl ether was added to 5 mmol of dimethylzinc in diethyl ether. The resulting solution was stirred for 1 hr at room temperature, followed by addition of 12.5 mmol of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. The mixture was stirred for an additional hour at room temperature and then filtered. The resulting white solid was dried at room temperature *in vacuo* and analyzed. *Anal.* Calcd for Li_3ZnH_5: Li, 22.9; Zn, 71.6; H, 5.53. Found: Li, 20.8; Zn, 71.5; H, 5.47; Al, 2.01. The molar ratio of Li:Zn:H:$LiAlH_4$ was 2.67:1.00:4.88:0.068. The filtrate contained 11.92 mmol of aluminum, no zinc, and 13.42 mmol of lithium. The molar ratio of Li:Al:Zn in the filtrate was 1.12:1.00:0.00. The amount of Li_3ZnH_5 recovered was 5 mmol of a theoretical 5 mmol. The X-ray powder diffraction data are given in Table I. Infrared analysis of the solid (Nujol mull) showed two strong bands at 400–950 (centered at 680 cm^{-1}) and 1400–1900 cm^{-1} (centered at 1500 cm^{-1}) and two moderate bands at 950–1100 (centered at 990 cm^{-1}) and 1150–1450 cm^{-1} (centered at 1280 cm^{-1}).

(d) Reaction of $LiAlH_4$ with $LiZn_2(CH_3)_5$ in Diethyl Ether. Attempted Preparation of $LiZn_2H_5$. Methyllithium (5 mmol) in diethyl ether was added to 10 mmol of dimethylzinc in diethyl ether. The resulting solution was stirred for 1 hr at room temperature; 12.5 mmol of $LiAlH_4$ in diethyl ether was added. A white precipitate appeared immediately. This mixture was then stirred for an additional hour and filtered. The solid which was slightly gray at this point was dried under vacuum at room temperature. *Anal.* Calcd for $LiZn_2H_5$: Li, 4.86; Zn, 91.6; H, 3.54. Found: Li, 5.08; Zn, 91.6; H, 3.45. The molar ratio of Li:Zn:H was 1.00:1.92:4.66. The filtrate contained 12.55 mmol of aluminum, 0.04 mmol of zinc, and 12.59 mmol of lithium. The amount of solid recovered was 5 mmol of a theoretical 5 mmol. The X-ray powder diffraction data are given in Table I.

(e) Reaction of $LiAlH_4$ with $LiZn_3(CH_3)_7$ in Diethyl Ether. Attempted Preparation of $LiZn_3H_7$. Dimethylzinc (15 mmol) in diethyl ether was added to 5 mmol of methyllithium in diethyl ether. The resulting solution was stirred for 1 hr at room temperature followed by addition of 17.5 mmol of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. This mixture was stirred for 1 hr and filtered. The solid, which had turned slightly gray, was dried under vacuum at room temperature. *Anal.* Calcd for $LiZn_3H_7$: Li, 3.30; Zn, 93.4; H, 3.36. Found: Li, 3.11; Zn, 93.6; H, 3.34. The molar ratio of Li:Zn:H was 1.00:3.20:7.37. The filtrate contained 18.02 mmol of aluminum, no zinc, and 18.20 mmol of lithium. The yield of solid was 100%. The X-ray powder diffraction data are given in Table I.

Reactions Involving $(CH_3)_2Zn$ with KH. (a) Reaction of KH (Excess) and $(CH_3)_2Zn$ in Diethyl Ether. Dimethylzinc (26.73 mmol) in diethyl ether was added to a slurry of 60.4 mmol of potassium hydride in diethyl ether. The slurry became hot immediately and solvent came to reflux. A solid was always present during the reaction. The mixture was stirred overnight at room temperature and filtered the next day. The resulting white solid was dried under vacuum at room temperature. The X-ray powder diffraction data are given in Table II. The filtrate showed a molar ratio of K:Zn of 0.92:1.00, but it contained only 0.59 mmol of zinc; *i.e.*, only 2.22% of the starting zinc was found in the filtrate. The solid was slurried for 3 hr in THF and then filtered. The residual solid was shown to be KH by X-ray powder diffraction and the filtrate had a molar ratio of K:Zn:CH_3:H of 0.98:1.00:2.14:0.39. The $KZn(CH_3)_2H$ formed cleaved THF at room temperature producing a soluble product.

(b) Reaction of AlH_3 with $KZn(CH_3)_2H$ in THF. Preparation of KZn_2H_5. Dimethylzinc (10 mmol) in THF was added to 10 mmol of a slurry of KH in THF at room temperature. The mixture was clear within 1 min. The mixture was quickly cooled to −80° to prevent ether cleavage and stirred an additional 2 hr. Next, 10 mmol of AlH_3 in THF was added at −80°. The bath was removed and the reaction mixture allowed to warm to room temperature. After 15 min a white precipitate began to form. The mixture was stirred an additional hour and filtered. The solid was dried under vacuum at room temperature. *Anal.* Calcd for KZn_2H_5: K, 22.4; Zn, 74.8; H, 2.88. Found: K, 23.2; Zn, 74.0; H, 2.79. The molar ratio of K:Zn:CH_3:H was 1.05:2.00:0.00:4.92. The filtrate contained 10.21 mmol of aluminum, no zinc, and 5.26

ble I. X-Ray Powder Patterns for Complex Metal Zinc Hydrides of Lithium

i_2ZnH_4 + Zn[a]		Li_2ZnH_4 + Zn[b]		Li_2ZnH_4 + Zn[c]		Li_2ZnH_4[d]		Li_3ZnH_5[e]		$LiZnH_3$[f]		"$LiZn_2H_5$"[g]		"$LiZn_3H_7$" + Zn[h]		Zn[i]		LiH[j]		ZnH_2[k]	
, Å	I/I_0[l]	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
25	m	4.25	m	4.22	mw	5.02	m	4.45	w	6.25	m	6.24	m	6.24	m					4.51	vw
83	m	3.85	m	3.85	w	4.69	w	2.84	s	5.02	w	4.45	s	4.45	s					4.23	s
67	w	3.69	mw	3.69	w	4.25	s	2.78	w	4.45	vs	4.30	m	3.24	m					3.80	vw
44	m	3.44	m	3.42	w	3.84	vs	2.64	m	4.30	m	3.26	s	3.10	m					3.40	m
95	m	2.95	m	3.25	vw	3.65	m	2.50	m	4.19	m	3.10	m	2.91	mw					2.97	vw
70	w	2.68	mw	2.95	mw	3.42	ms	1.91	w	3.81	ms	2.94	m	2.81	m					2.828	vw
47	m	2.46	ms	2.73	w	2.95	ms	1.79	w	3.65	w	2.81	m	2.45	m	2.473	m			2.608	w
43	m	2.29	ms	2.46	ms	2.71	mw	1.63	mw	3.42	mw	2.50	m	2.31	mw			2.357	m	2.468	vw
29	w	2.09	vs	2.29	ms	2.46	s	1.50	m	3.24	vs	2.41	m	2.16	mw	2.308	m			2.387	m
12	w	1.90	vw	2.09	s	2.42	s	1.385	w	3.10	m	2.24	w	2.09	s					2.290	m
08	m	1.83	vw	1.68	m	2.32	m			2.94	s	2.17	mw	1.98	w	2.091	s			2.225	m
95	w	1.68	m	1.34	m	2.26	mw			2.81	s	2.07	w	1.96	w			2.041	s	2.135	w
84	w	1.33	m	1.33	m	2.24	mw			2.50	mw	1.98	w	1.75	w					2.085	w
68	w	1.23	w	1.23	w	2.12	m			2.45	m	1.95	w	1.68	w					2.017	vw
60	w	1.17	m	1.17	m	2.07	w			2.41	m	1.75	w	1.33	w	1.687	m			1.905	w
17	w	1.15	w	1.15	w	1.99	m			2.31	w	1.60	w	1.17	w					1.764	w
90	w	1.12	m	1.12	m	1.91	m			2.24	mw	1.495	w	1.12	w			1.444	m	1.688	vw
865	w	1.09	w	1.09	w	1.84	m			2.16	mw	1.25	vw			1.342	m	1.444		1.603	vw
		1.04	w	1.04	w	1.79	m			2.12	w					1.332	m			1.562	vw
		0.941	w	0.941	w	1.70	w			2.06	w					1.237	w	1.231	mw	1.486	vw
		0.907	w	0.907	w	1.67	w			1.98	mw					1.173	m	1.178	w	1.464	vw
		0.904	w	0.905	w	1.64	w			1.94	mw					1.154	w			1.416	vw
		0.903	w	0.870	w	1.60	m			1.90	mw					1.124	w			1.336	vw
		0.870	w	0.856	w	1.57	w			1.84	w					1.091	w			1.305	vw
		0.856	w	0.855	w	1.54	w			1.75	mw					1.046	w			1.295	vw
		0.854	w	0.821	w	1.52	w			1.64	w							1.020	vw	1.259	vw
		0.821	w	0.819	w	1.50	w			1.60	m							0.9374	w	1.219	vw
		0.818	w			1.48	m			1.52	w							0.9130	w	1.172	vw
						1.47	M			1.495	w							0.8335	w	1.157	vw
						1.456	w			1.44	w							0.7859	vw	1.123	vw
						1.44	w			1.244	w										
						1.397	w														
						1.36	w														
						1.34	w														
						1.32	w														
						1.29	w														
						1.21	w														

[a] $LiZn(sec\text{-}C_4H_9)_2H + LiAlH_4$ in THF. [b] $LiZn(CH_3)_2H + LiAlH_4$ in THF. [c] $LiZn_2(CH_3)_4H + LiAlH_4$ in THF. [d] $Li_2Zn(CH_3)_4 + LiAlH_4$ in diethyl ether. [e] $Li_3Zn(CH_3)_5 + LiAlH_4$ in diethyl ether. $LiZn(CH_3)_3 + LiAlH_4$ in diethyl ether. [g] $LiZn_2(CH_3)_5 + LiAlH_4$ in diethyl ether. [h] $LiZn_3(CH_3)_7 + LiAlH_4$ in diethyl ether. [i] ASTM file. [j] ASTM file. [k] $LiAlH_4$-$(C_2H_5)_2Zn$, see ref 5. [l] w, weak; n, medium; s, strong; v, very.

Table II. X-Ray Powder Patterns for Complex Metal Zinc Hydrides of Potassium

$KZn(CH_3)_2$ + KH[a]		KH[b]		K_2ZnH_4[c]		ZnH_2[d]		KZn_2H_5[e]		KZn_2H_5[f]		"KZn_3H_7"[g]		$KZnH_3$[h]	
d, Å	I/I_0[i]	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
6.10	mw			5.10	w	4.51	vw	6.03	s	6.03	s	6.02	ms	6.25	ms
5.30	mw			4.26	m	4.23	s	4.10	mw	4.08	mw	4.06	mw	5.60	vw
4.05	mw, d			3.89	w	3.80	vw	3.72	mw	3.72	w	3.72	w	5.10	s
3.89	mw, d			3.62	vw	3.40	m	3.36	vs	3.36	vs	3.36	vw	4.40	vw
3.59	ms, d			3.47	m	2.97	vw	3.01	m	3.02	mw	3.02	mw	3.71	vw
3.40	ms, d			3.24	w	2.828	vw	2.67	vw	2.69	w	2.79	vw	3.59	m
3.27	s	3.30	vs	3.09	s	2.608	w	2.59	vw	2.61	w	2.69	vw	3.43	vs
2.83	s	2.86	s	2.940	s	2.468	vw	2.42	s	2.43	s	2.60	vw	3.31	m
2.75	w			2.744	w	2.387	m	2.35	s	2.34	s	2.43	s	3.11	ms
2.45	m			2.568	vvw	2.290	m	2.18	m	2.18	m	2.35	s	2.80	s
2.10	w			2.354	w	2.225	m	2.14	vw	2.02	w	2.28	vw	2.71	vs
2.00	ms	2.02	s	2.128	w	2.135	w	2.00	vw	1.93	ms	2.19	m	2.58	s
1.71	ms	1.72	s	1.946	w	2.085	w	1.93	ms	1.85	m	2.09	m	2.33	s
1.64	w	1.65	m	1.814	w	2.017	vw	1.85	m	1.80	m	2.03	vw	2.29	w
1.57	vw			1.734	w	1.905	w	1.80	m	1.68	m	2.01	vw	2.18	w
1.43	w	1.43	m	1.648	vw	1.764	w	1.68	m	1.53	w	1.93	ms	2.15	vw
1.30	w	1.31	m	1.624	vw	1.688	vw	1.54	w	1.490	m	1.86	m	2.12	vw
1.27	w	1.28	m	1.571	w	1.630	vw	1.49	m	1.432	w	1.81	m	2.07	m
1.16	w	1.17	m	1.488	w	1.562	vw	1.431	w	1.415	w	1.69	m	2.03	w
1.09	w	1.10	m	1.470	w	1.486	vw	1.414	w	1.371	w	1.65	vw	1.94	vw
0.96	w	1.01	w	1.384	vw	1.464	vw	1.371	mw	1.351	w	1.53	vw	1.90	ms
				1.213	w	1.416	vw	1.355	mw	1.322	w	1.49	m	1.86	w
						1.336	vw	1.328	w	1.270	w	1.435	mw	1.85	vw
						1.305	vw	1.269	vw	1.234	vw	1.419	w	1.79	m
						1.295	vw	1.238	vw	1.222	w	1.361	mw	1.77	m
						1.219	vw	1.222	w	1.191	vw	1.355	mw	1.73	m
						1.172	vw	1.176	w	1.175	w	1.321	vw	1.72	w
						1.157	vw	1.151	vw	1.154	vw	1.300	vw	1.69	m
						1.123	vw	1.111	w	1.111	w	1.271	vvw	1.66	w
						1.042	vw	1.076	vw	1.078	w	1.239	vvw	1.64	w
								1.060	vw	1.057	w	1.223	w	1.595	m
								1.005	vw	1.003	vw	1.221	vw	1.57	w
								0.983	vw	0.986	vw	1.175	vw	1.55	w
								0.922	vw	0.022	vw	1.152	vw	1.455	mw
								0.888	vw	0.906	vw	1.111	w	1.370	mw
												1.079	w	1.325	mw
												1.059	w		

[a] Excess KH + $(CH_3)_2Zn$ in diethyl ether. [b] ASTM files. [c] KH + $(sec\text{-}C_4H_9)_2Zn$ in benzene, see ref 5. [d] $LiAlH_4$ + $(C_2H_5)_2Zn$, see ref 5. [e] $KZn(CH_3)_2H$ + AlH_3 in tetrahydrofuran. [f] $KZn_2(CH_3)_4H$ + AlH_3 in tetrahydrofuran. [g] $KZn_3(CH_3)_6$ + AlH_3 in tetrahydrofuran. [h] $KZn(CH_3)_2H$ + $LiAlH_4$ in tetrahydrofuran. [i] w, weak; m, medium; s, strong; v, very; d, diffused.

mmol of potassium. The molar ratio of K:Al in the filtrate was 1.03:2.00. The X-ray powder diffraction pattern of the solid is given in Table II.

(c) **Reaction of $LiAlH_4$ with $KZn(CH_3)_2H$ in THF. Preparation of $KZnH_3$.** Dimethylzinc (10 mmol) in THF was added to 10 mmol of KH slurried in THF. The clear solution which resulted was cooled to −80° and stirred for 1 hr. Next, 10 mmol of lithium aluminum hydride in THF was added to the solution. The solution was warmed to room temperature and a white precipitate resulted. This mixture was stirred for 1 hr and filtered. The resulting white solid was dried under vacuum at room temperature. *Anal.* Calcd for $KZnH_3$: K, 36.4; Zn, 60.8; H, 2.81. Found: K, 36.6; Zn, 60.5; H, 2.86. The molar ratio of Li:K:Zn:H was 0.00:1.01:1.00:2.96. The filtrate contained 9.64 mmol of aluminum, no zinc, no potassium, and 9.75 mmol of lithium. The molar ratio of K:Li:Al in the filtrate was 0.00:1.01:1.00. The X-ray powder diffraction pattern of the solid is given in Table II.

(d) **Reaction of AlH_3 with $KZn_2(CH_3)_4H$ in THF. Preparation of KZn_2H_5.** Dimethylzinc (20 mmol) in THF was added to 10 mmol of KH slurried in THF. A clear solution resulted even before all the dimethylzinc could be introduced. The solution was quickly cooled to −80° and stirred for an additional hour at this temperature. Next, 14.82 mmol of AlH_3 in THF was added to the solution at −80°. A faint white precipitate appeared immediately. The bath was removed and the mixture stirred for 1 hr and then filtered. The solid was dried under vacuum at room temperature. *Anal.* Calcd for KZn_2H_5: K, 22.4; Zn, 74.8; H, 2.88. Found: K, 21.5; Zn, 75.8; H, 2.79. The molar ratio of K:Zn:H was 1.00:2.10:5.04. The filtrate contained 16.96 mmol of aluminum, no zinc, and 0.83 mmol of potassium. The molar ratio of K:Al in the filtrate was 0.098:2.00. The X-ray powder diffraction pattern of

(e) **Reaction of AlH_3 with $KZn_3(CH_3)_6H$ in THF. Attempted Preparation of KZn_3H_7.** Dimethylzinc (15 mmol) in THF was added to 5 mmol of KH slurried in THF. The clear solution which resulted was cooled to −80° and stirred for 1 hr. Next, 15 mmol of AlH_3 in THF was added to the solution at −80°. The mixture was allowed to warm to room temperature (a white precipitate formed in the process), stirred for 1 hr, and then filtered. The solid was dried under vacuum at room temperature. *Anal.* Calcd for KZn_3H_7: K, 16.1; Zn, 80.9; H, 2.92. Found: K, 15.0; Zn, 82.1; H, 2.92. The molar ratio of K:Zn:H was 1.00:3.29:7.56. The filtrate contained 16.09 mmol of aluminum, no zinc, and 0.44 mol of potassium. The molar ratio of K:Al in the filtrate was 0.055:2.00. The X-ray diffraction pattern of the solid, which is given in Table II, showed lines due to KZn_2H_5 only.

Reactions Involving $(CH_3)_2Zn$ with NaH. (a) Reaction of $NaAlH_4$ with $NaZn(CH_3)_2H$ in THF. Preparation of $NaZnH_3$. Dimethylzinc (10 mmol) in THF was added to 10 mmol of NaH slurried in THF. The mixture was quickly cooled to −80° and stirred at that temperature until the Na:Zn ratio in the supernatnat was 1:1. At this point, 5 mmol of the supernatant solution [$NaZn(CH_3)_2H$] was allowed to react with 5 mmol of sodium aluminum hydride in THF. A white precipitate appeared within minutes. The mixture was stirred 20 min and filtered. The resulting white solid was dried under vacuum at room temperature. *Anal.* Calcd for $NaZnH_3$: Na, 25.2; Zn, 71.5; H, 3.30. Found: Na, 25.2; Zn, 71.6; H, 3.24. The molar ratio of Na:Zn:H was 1.00:1.00:2.94. The X-ray powder diffraction pattern is given in Table III. The filtrate contained 4.62 mmol of aluminum, 0.47 mmol of zinc, and 5.06 mmol of sodium.

(b) **Reaction of AlH_3 and $NaZn(CH_3)_2H$ in THF. Preparation of $NaZn_2H_5$.** Dimethylzinc (5 mmol) in THF was added to 5 mmol

of AlH_3 in THF was added at room temperature. An off-white precipitate appeared. The mixture was stirred for 2 hr and filtered. The solid was dried under vacuum at room temperature. *Anal.* Calcd for $NaZn_2H_5$: Na, 14.5; Zn, 82.4; H, 3.15. Found: Na, 15.2; Zn, 81.7; H, 3.01. The molar ratio of Na:Zn:H was 1.06:2.00:4.83. The molar ratio of Na:Al:Zn in the filtrate was 1.03:2.00:0.061. The X-ray powder diffraction pattern of the solid is given in Table III.

(c) Reaction of $NaZn(CH_3)_2H$ with $LiAlH_4$ in THF. Preparation of $NaZnH_3$. To 6 mmol of $NaZn(CH_3)_2H$ in THF at −80° was added 6 mmol of $LiAlH_4$ in THF. This mixture was allowed to warm to room temperature during which time a white precipitate resulted. The resulting white solid was filtered and dried at room temperature under vacuum. The molar ratio of Na:Zn:H in the solid was 1.00:1.00:2.75. The X-ray powder diffraction pattern, given in Table III, was identical with that of $NaZnH_3$. The filtrate contained 5.82 mmol of aluminum and 3.04 mmol of zinc.

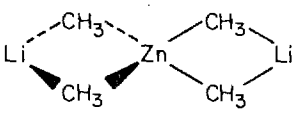
(d) Reaction of $NaAlH_4$ with $NaZn_2(CH_3)_4H$ in THF. Attempted Preparation of $NaZn_2H_5$. Dimethylzinc (20 mmol) in THF was added to 10 mmol of NaH slurried in THF. The mixture was quickly cooled to −80° and stirred until the Na:Zn ratio in the supernatant was 0.50:1.00. At this point, 5 mmol of the supernatant [$NaZn_2(CH_3)_4H$ solution] was allowed to react with 10 mmol of sodium aluminum hydride in THF. A white precipitate appeared within minutes. The mixture was stirred for 1 hr and filtered. The resulting white solid was dried at room temperature under vacuum. The molar ratio of Na:Zn:H in the solid was 1.00:1.00:2.90. The X-ray powder diffraction pattern, given in Table III, was identical with that for $NaZnH_3$. The filtrate contained 10.00 mmol of aluminum, 3.06 mmol of zinc, and 9.50 mmol of sodium.

(e) Reaction of NaH with $(sec\text{-}Bu)_2Zn$ in THF. Attempted Preparation of $Na_2Zn(sec\text{-}C_4H_9)_2H_2$ and Na_2ZnH_4. To 10 mmol of NaH slurried in THF was added 5 mmol of $(sec\text{-}Bu)_2Zn$ in THF. The mixture was stirred at room temperature for 1 day (a solid remained throughout this period) and then filtered. The solid was dried under vacuum at room temperature. The molar ratio of Na:H:Zn in the solid was found to be 1.00:1.03:0.070. The X-ray powder diffraction pattern and vacuum dta–tga showed that the solid was mostly NaH. The filtrate, which contained sodium and zinc in a molar ratio of 1.11:1.00, when allowed to react with $NaAlH_4$, yielded $NaZnH_3$ only.

Results and Discussion

While it is known that metal hydrides of the main group elements can be prepared by the reduction of a metal alkyl with lithium aluminum hydride,[14] there have been no reports of the application of this simple reaction to the synthesis of new complex metal hydrides. When we found that the "ate" complexes of zinc [*i.e.*, $LiZn(sec\text{-}C_4H_9)_2H$] are cleaved by ether solvents, at the temperatures necessary to carry out hydrogenolysis (75–150°) to the corresponding hydride, it was necessary to develop another method of reduction that could be carried out at lower temperature. It was found that $LiAlH_4$, $NaAlH_4$, or AlH_3 will reduce the "ate" complex to the corresponding hydride rapidly at room temperature.

Li_2ZnH_4. The "ate" complex $Li_2Zn(CH_3)_4$, lithium tetramethylzincate, first prepared by Hurd[15] in 1948, has been characterized both by nmr[16] and X-ray crystallography.[17] Its structure is shown below.



When $Li_2Zn(CH_3)_4$ and $LiAlH_4$ were allowed to react, Li_2ZnH_4 was obtained in 100% yield according to eq 7. The X-ray powder diffraction pattern of Li_2ZnH_4 (Table I)

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(15) D. J. Hurd, *J. Org. Chem.*, 13, 711 (1948).
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Table III. X-Ray Powder Patterns for Complex Metal Zinc Hydrides of Sodium

$NaZnH_3$ [a]		$NaZnH_3$ [b]		$NaZnH_3$ [c]		NaH [d]		$NaZn_2H_5$ [e]	
d, Å	I/I_0 [f]	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
8.70	vw	8.70	vw					5.84	m
5.99	w	5.99	w	5.87	vw			4.89	s
4.90	vs	4.90	vs	4.90	s			3.29	vs
4.39	w	4.40	w					3.09	m
3.98	w	3.91	w					2.83	s
3.30	m	3.52	w					2.50	w
3.11	vs	3.27	ms	3.26	m			2.44	m
2.91	m	3.11	vs	3.11	vs			2.36	m
2.81	w	2.92	m					2.26	m
2.63	mw	2.81	m	2.84	w	2.83	s	2.15	w
2.56	m	2.62	w					2.09	w
2.49	ms	2.56	ms					2.01	mw
2.43	m	2.49	s	2.51	m	2.44	ms	1.70	m
2.38	vw	2.44	m	2.45	w			1.62	w
2.26	w	2.25	w	2.38	vw			1.55	w
2.22	w	2.20	w	2.28	vw			1.50	w
2.15	w	2.15	vw	2.23	vw			1.465	w
2.07	w	2.07	w	2.16	vvw			1.375	w
1.96	mw	2.02	vw	2.09	vw			1.351	w
1.83	mw	1.97	mw	2.02	vvw			1.301	vw
1.78	w	1.84	w	1.98	w				
1.72	vw	1.78	w	1.79	vvw	1.73	ms		
1.66	mw	1.70	w	1.70	vvw	1.47	ms		
1.61	mw	1.66	w	1.67	vw	1.41	m		
1.58	vw	1.61	mw	1.62	w	1.22	mw		
1.53	mw	1.58	w	1.55	w	1.12	m		
1.49	vw	1.53	mw	1.47	vvw	1.09	m		
1.38	vw	1.49	vw	1.35	vw	0.996	m		
1.34	w	1.47	vw			0.939	m		
1.22	vw	1.37	vw			0.863	mw		
1.06	vw	1.34	vw			0.825	m		
1.00	vw	1.22	vw			0.813	m		
		1.00	vvw						

[a] $NaZn(CH_3)_2H + NaAlH_4$ in tetrahydrofuran. [b] $NaZn(CH_3)_4H + NaAlH_4$ in tetrahydrofuran. [c] See ref 11, made by thermally decomposing $NaZn_2(CH_3)_2H_3$. [d] ASTM file. [e] $NaZn(CH_3)_2H + AlH_3$ in tetrahydrofuran. [f] w, weak; m, medium; s, strong; v, very.

$$Li_2Zn(CH_3)_4 + 2LiAlH_4 \rightarrow Li_2ZnH_4 + 2LiAl(CH_3)_2H_2 \quad (7)$$

contains no lines due to LiH or ZnH_2; therefore, the product is not a physical mixture of the two simple hydrides. On the other hand, both the powder diffraction pattern and infrared spectrum of Li_2ZnH_4 were similar to that found for K_2ZnH_4 (Table II). The infrared spectrum of the solution that remained after filtration of Li_2ZnH_4 showed that the aluminum-containing species was $LiAl(CH_3)_2H_2$. Therefore, complete exchange of the methyl groups from zinc to aluminum had occurred. The structure of Li_2ZnH_4 might be similar to that of $Li_2Zn(CH_3)_4$, however, due to the insolubility of the hydride; association, ir, and nmr data are not available to establish this point.

Oddly enough, the reaction of either $LiZn(sec\text{-}C_4H_9)_2H$, $LiZn(CH_3)_2H$, or $LiZn_2(CH_3)_4H$ with $LiAlH_4$ in tetrahydrofuran also yields Li_2ZnH_4. The X-ray powder diffraction patterns of Li_2ZnH_4 from each of these reactions (Table I) show weak to moderate lines for Li_2ZnH_4 and strong lines for zinc metal. It was found that the presence of a large excess of tetrahydrofuran with any of the complex metal hydrides discussed here always greatly increased the rate of decomposition to zinc metal at room temperature. After this trend had been noticed, all solid products were filtered as quickly as possible. When Li_2ZnH_4 was prepared from $Li_2Zn(CH_3)_4$, no zinc metal lines were observed when the compound was stirred in the reaction mixture for only 1 hr before filtration.

The route by which Li_2ZnH_4 is formed from $LiZn(sec\text{-}$

$(sec\text{-}C_4H_9)_3H$, $LiZn(CH_3)_2H$, and $LiZn_2(CH_3)_4H$ is not clear, specially in the case of $LiZn_2(CH_3)_4H$. A reasonable explanation for the formation of Li_2ZnH_4 from $LiZn(sec\text{-}C_4H_9)_2H$ or $LiZn(CH_3)_2H$ is that $LiAlH_4$ undergoes hydrogen-alkyl group exchange with the $LiZnR_2H$ compound in a stepwise fashion. After the first alkyl exchange step, it is suggested that $LiZnRH_2$ (where $R = CH_3$ or $sec\text{-}C_4H_9$) forms which could then disproportionate to Li_2ZnH_4 and ZnR_2 faster than it reacts with $LiAlRH_3$ (eq 8).

$$2LiZn(CH_3)_2H_2 \rightarrow Li_2ZnH_4 + (CH_3)_2Zn \quad (8)$$

This explanation is supported by elemental analysis of the reaction mixtures from reduction of $LiZn(sec\text{-}C_4H_9)_2H$ and $LiZn(CH_3)_2H$ with $LiAlH_4$. The solid product from the reaction of $LiZn(sec\text{-}C_4H_9)_2H$ with $LiAlH_4$ had a molar ratio of Li:Zn:H of 2:1:4. The filtrate contained one-half of the initial amount of zinc. Thus, the solid (Li_2ZnH_4) contained the other half. This is consistent with the disproportionation of an intermediate complex to equimolar amounts of di-*sec*-butylzinc and Li_2ZnH_4. Evidently, di-*sec*-butylzinc was not reduced to zinc hydride by the intermediate aluminum hydride species, $LiAl(sec\text{-}C_4H_9)H_3$. The solid from the reaction of $LiZn(CH_3)_2H$ with $LiAlH_4$ had a molar ratio of Li:Zn:H of 1:1:3. The filtrate contained very little of the starting zinc compound and the X-ray powder diffraction pattern showed only lines for Li_2ZnH_4 and zinc metal. Thus, the solid product must be a mixture of Li_2ZnH_4 and ZnH_2, where the ZnH_2 comes from reduction of $(CH_3)_2Zn$ with $LiAl(CH_3)H_3$. A situation similar to this was encountered by Coates[18] in the preparation of $LiBeH_3$. The X-ray powder diffraction pattern of the compound contained lines due to Li_2BeH_4 only, but the analysis showed a molar ratio of Li:Be:H of 1:1:3. Coates concluded that the product was an equimolar mixture of Li_2BeH_4 and BeH_2.

The mechanism of formation of Li_2ZnH_4 by reaction of $LiZn_2(CH_3)_4H$ with $LiAlH_4$ is not as well understood. Even less understandable is the reason why $LiZn_2(CH_3)_4H$ reacts so slowly with $LiAlH_4$. It took 5 days for essentially all the zinc to appear in the solid whereas most of the "ate" complexes used in this work react with $LiAlH_4$ instantaneously to yield solid products containing all of the original zinc. The solid did contain Li:Zn in a ratio of 1:2, but the active hydrogen was very low indicating considerable decomposition. It is possible that the initial reduction product was $LiZn_2H_5$, which decomposed to Li_2ZnH_4 and ZnH_2. A more reasonable reaction path consists of a slow stepwise exchange of a methyl group of $LiZn_2(CH_3)_4H$ to the intermediate complex, $LiZn_2(CH_3)_3H_2$, which could then disproportionate to Li_2ZnH_4 and $(CH_3)_2Zn$ according to eq 9.

$$LiZn_2(CH_3)_4H + LiAlH_4 \rightarrow LiZn_2(CH_3)_3H_2 \rightarrow {}^1/_2Li_2ZnH_4 + {}^3/_2(CH_3)_2Zn \quad (9)$$

The $(CH_3)_2Zn$ would then presumably be reduced rapidly in the presence of $LiAlH_4$ to ZnH_2. The major part of the decomposition is probably due to decomposition of ZnH_2.

The vacuum dta-tga of Li_2ZnH_4 is shown in Figure 2. Li_2ZnH_4 decomposes evolving noncondensable gases at 136 and 310°. The thermal effect for the first gas evolution contains a sharp exotherm superimposed on a broad deep endotherm. The thermal effect for the next gas evolution is a small endotherm. The ratio of weight loss for the two gas evolutions is 1:1. The first gas evolution is attributed to decomposition of Li_2ZnH_4 to LiH and ZnH_2 with simultaneous decomposition of ZnH_2. The last endotherm is due to the decomposition of LiH. An X-ray powder diffraction pattern taken after the first step showed the presence of LiH and Zn metal. The steps involved in the decomposition are shown below.

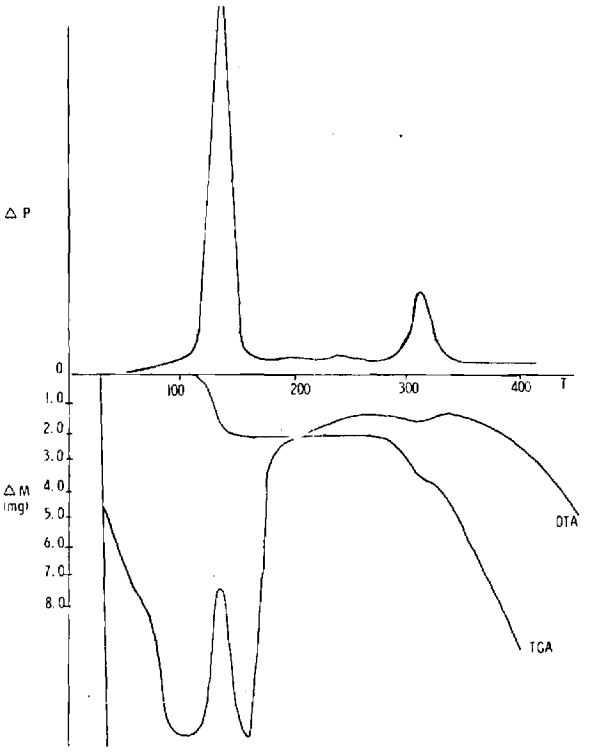


Figure 2. Vacuum dta-tga of Li_2ZnH_4.

step 1: $Li_2ZnH_4 \rightarrow 2LiH + Zn + H_2$

step 2: $2LiH \rightarrow 2Li + H_2$

Li_3ZnH_5. In their low-temperature nmr work on the system CH_3Li-$(CH_3)_2Zn$, Seitz and Brown[16] reported the existence of two complexes, $Li_2Zn(CH_3)_4$ and $Li_3Zn(CH_3)_5$. Since reduction of $Li_2Zn(CH_3)_4$ with $LiAlH_4$ yields Li_2ZnH_4, reduction of $Li_3Zn(CH_3)_5$ with $LiAlH_4$ should provide a convenient route to Li_3ZnH_5 (eq 10).

$$Li_3Zn(CH_3)_5 + {}^5/_2LiAlH_4 \rightarrow Li_3ZnH_5 + {}^5/_2LiAl(CH_3)_2H_2 \quad (10)$$

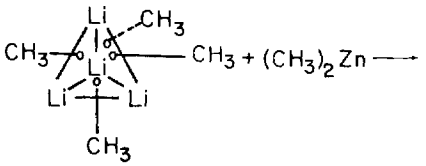
The reaction of $Li_3Zn(CH_3)_5$ with $LiAlH_4$ in diethyl ether at room temperature gave Li_3ZnH_5 in 100% yield. The product contained a small amount of $LiAlH_4$ which precipitated with the product. The X-ray powder diffraction pattern (Table I) did not contain any lines due to Li_2ZnH_4, ZnH_2, or LiH; therefore, the product of the reaction is not a physical mixture. The infrared spectrum contained two strong and two moderate bands. The two strong bands are centered at 680 and 1550 cm^{-1}. The two moderate bands are centered at 990 and 1280 cm^{-1}. Although the structure of Li_3ZnH_5 might be similar to that proposed by Brown[16] for $Li_3Zn(CH_3)_5$, because of the insolubility of the hydride, molecular association, ir, and nmr data could not be obtained to establish this point.

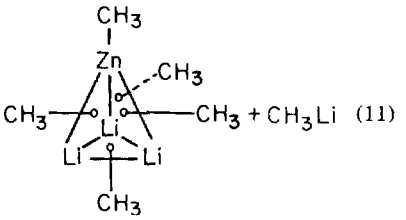
The vacuum dta-tga of this compound, run several months after it was originally prepared, was similar to that observed for Li_2ZnH_4. At this point it was thought that Li_3ZnH_5 decomposed slowly over a period of months to Li_2ZnH_4 and LiH; however, subsequent attempts to reprepare Li_3ZnH_5 have failed. In each case the product was a mixture of Li_2ZnH_4 and LiH. This is the only complex metal hydride reported in this work, the preparation of which could not

(18) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 628 (1968).

be reproduced. In spite of this result, the original data indicated the unequivocal formation of Li_3ZnH_5.

$LiZnH_3$. $Li_3Zn(CH_3)_5$ has been reported[16] to be formed in diethyl ether by substitution of one dimethylzinc molecule for one methyllithium unit in the methyllithium tetramer (eq 11). $LiZn(CH_3)_3$ could then be formed by substitution





(11)

of two methyllithium units in the methyllithium tetramer by two molecules of dimethylzinc. $LiZn(CH_3)_3$ formed in this way should provide an excellent precursor to $LiZnH_3$.

The reaction of a 1:1 mixture of methyllithium and dimethylzinc with $LiAlH_4$ in diethyl ether did produce $LiZnH_3$ (eq 12 and 13). The X-ray powder diffraction pattern of

$$^1/_2(LiCH_3)_4 + 2Zn(CH_3)_2 \rightarrow 2LiZn(CH_3)_3 \quad (12)$$

$$LiZn(CH_3)_3 + {}^3/_2LiAlH_4 \rightarrow LiZnH_3 + {}^3/_2LiAl(CH_3)_2H_2 \quad (13)$$

$LiZnH_3$ (Table I) was very different from that of Li_2ZnH_4 or Li_3ZnH_5 and did not contain any lines in common with LiH or ZnH_2. Little information concerning the structure of $LiZnH_3$ is available since the compound is not soluble enough to obtain molecular association and nmr data.

The vacuum dta-tga of $LiZnH_3$ is shown in Figure 3. It contained noncondensable gas evolutions at 97, 136, and 290°. The gas evolution at 97° was accompanied by a strong exothermal effect and is probably due to disproportionation of $LiZnH_3$ to Li_2ZnH_4 and ZnH_2, with simultaneous decomposition of ZnH_2. The decomposition of ZnH_2 normally occurs between 90 and 100°. The fact that the next two gas evolutions correspond to those accompanying decomposition of Li_2ZnH_4 supports this proposal.

The thermal decomposition of $LiZnH_3$ is believed to occur in essentially three steps.

step 1: $2LiZnH_3 \rightarrow Li_2ZnH_4 + ZnH_2$

$ZnH_2 \rightarrow Zn + H_2$

step 2: $Li_2ZnH_4 \rightarrow 2LiH + Zn + 2H_2$

step 3: $2LiH \rightarrow 2Li + H_2$

The first step is slow compared to the second which shows ZnH_2 decomposing very rapidly once formed. The decomposition of Li_2ZnH_4 occurs at higher temperatures.

$LiZn_2H_5$ and $LiZn_3H_6$. The 1:2 and 1:3 mixtures of methyllithium and dimethylzinc were allowed to react with $LiAlH_4$ in diethyl ether. The solid compounds obtained had Li:Zn:H ratios of 1:2:5 and 1:3:7. However, the X-ray powder diffraction patterns of the solids (Table I) contained lines due only to $LiZnH_3$. Thus, the solid compounds are 1:1 and 1:2 mixtures of $LiZnH_3$ and ZnH_2.

$KZn(CH_3)_2H$ and $KZn_2(CH_3)_4H$. In contrast to the reaction of di-*sec*-butylzinc with KH which yields K_2ZnH_4 directly, KH and dimethylzinc react in 1:1 ratio in either

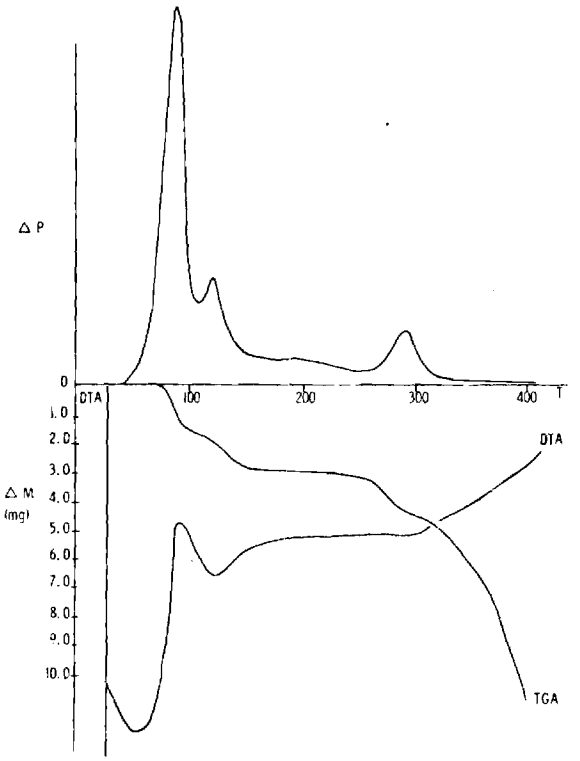


Figure 3. Vacuum dta-tga of $LiZnH_3$.

quantitative yield. This complex had not been prepared previously; however, its properties were found to be analogous to those of $LiZn(CH_3)_2H$ and $NaZn(CH_3)_2H$ which had been prepared earlier by Shriver.[9] Like the lithium and sodium complexes, $KZn(CH_3)_2H$ was insoluble in diethyl ether but soluble in tetrahydrofuran. Reaction of $KZn(CH_3)_2H$ was found to take place with another molecule of $(CH_3)_2Zn$ to give $KZn_2(CH_3)_4H$, which like the lithium and sodium complexes decomposed to $KZn(CH_3)_2H$ and $(CH_3)_2Zn$ when an attempt was made to isolate it as a solid.

KZn_2H_5. The reaction of $KZn(CH_3)_2H$ with AlH_3 in tetrahydrofuran (AlH_3 was chosen as reducing agent because of the possibility of alkali metal exchange if $LiAlH_4$ were used) was selected as a convenient route to $KZnH_3$. However, the reaction readily proceeds to give KZn_2H_5 (eq 14)

$$2KZn(CH_3)_2H + 2AlH_3 \rightarrow KZn_2H_5 + KAl(CH_3)_2H_2 \cdot Al(CH_3)_2H \quad (14)$$

in quantitative yield. The X-ray powder diffraction pattern for KZn_2H_5 (Table II) contains no lines due to KH, ZnH_2, or K_2ZnH_4. The infrared spectrum of the filtrate containing the $KAl(CH_3)_2H_2 \cdot Al(CH_3)_2H$ showed a broad band in the Al-H stretching region centered at 1618 cm^{-1}. Me_2AlH absorbs at 1750 cm^{-1} in THF; thus, the species is not a mixture of $Al(CH_3)_2H$ and $KAl(CH_3)_2H_2$ in solution.

KZn_2H_5 was also formed by reduction of $KZn_2(CH_3)_4H$ with AlH_3 in tetrahydrofuran (eq 15). In this reaction very

$$KZn_2(CH_3)_4H + 2AlH_3 \rightarrow KZn_2H_5 + 2Al(CH_3)_2H \quad (15)$$

little potassium was found in the filtrate. The X-ray powder diffraction pattern of KZn_2H_5 obtained from this reaction is shown in Table II.

The vacuum dta-tga of KZn_2H_5 is shown in Figure 4. Large noncondensable gas evolutions occurred at 125, 223, and 267°. The ratio of the weight loss during the first gas evolution to that during the second was 3:1. The thermal effect for the first gas evolution showed a sharp endotherm superimposed on a broad exotherm. The exotherm is be-

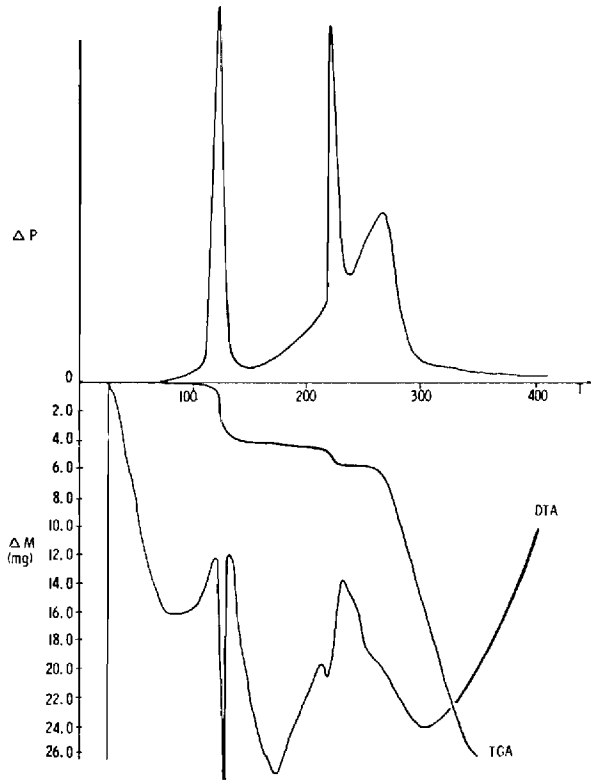


Figure 4. Vacuum dta-tga of KZn_2H_5.

lieved to be due to decomposition of KZn_2H_5 to $KZnH_3$ and ZnH_2 with simultaneous decomposition of ZnH_2 to Zn and H_2. The endotherm is believed to be due to disproportionation of $KZnH_3$ to K_2ZnH_4 and ZnH_2 with simultaneous decomposition of the ZnH_2. The thermal effects for the second and third gas evolutions were endothermal. The second gas evolution is due to the decomposition of K_2ZnH_4 to KH and ZnH_2 with simultaneous decomposition of ZnH_2. The third gas evolution is due to decomposition of KH. The mechanism of decomposition, shown in the three steps below, is supported by X-ray powder diffraction data, taken after the first two stages of gas evolution. The X-ray powder pattern taken after the first step showed lines for K_2ZnH_4 and Zn metal only. The X-ray powder pattern taken after the second step showed lines for KH and Zn metal. More evidence is provided by the fact that the ratio of the weight loss in step 1 to that in step 2 should be 3, which is what was found.

step 1: $KZn_2H_5 \rightarrow KZnH_3 + Zn + H_2$

$2KZnH_3 \rightarrow K_2ZnH_4 + Zn + H_2$

step 2: $K_2ZnH_4 \rightarrow 2KH + Zn + H_2$

step 3: $KH \rightarrow K + {}^1/_2H_2$

In order to substantiate that steps 2 and 3 are the only steps involved in the decomposition of K_2ZnH_4, the dta-tga of K_2ZnH_4 was investigated. The vacuum dta-tga shown in Figure 5 contained one very broad peak at 285° with shoulders at 200 and 237° indicative of the evolution of a noncondensable gas. Further information concerning the decomposition of K_2ZnH_4 by observing the dta-tga under argon flush is shown in Figure 6. The dta-tga contained three well-separated weight losses with corresponding endotherms at 150, 266, and 355°. This differs somewhat from the dta-tga for K_2ZnH_4 obtained, under argon, in our earlier report.[8] In the earlier work, K_2ZnH_4 was reported to have lost all solvent before 80° and have endothermal de-

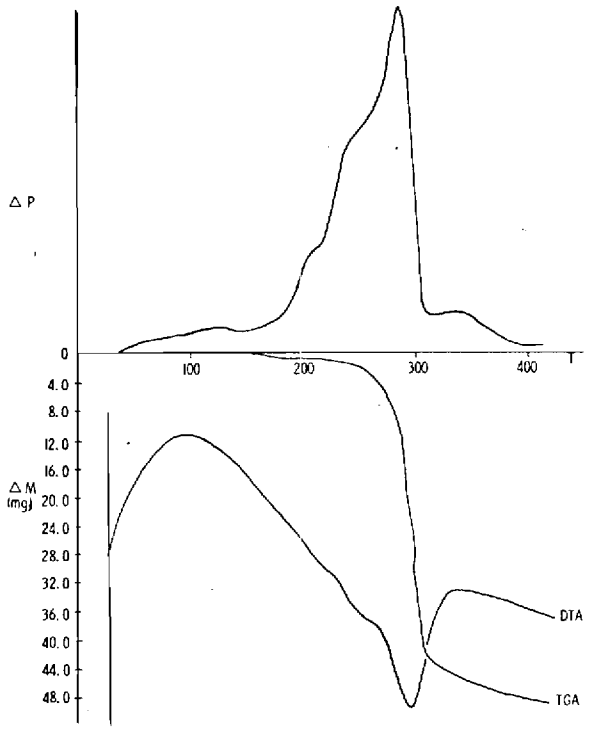


Figure 5. Vacuum dta-tga of K_2ZnH_4.

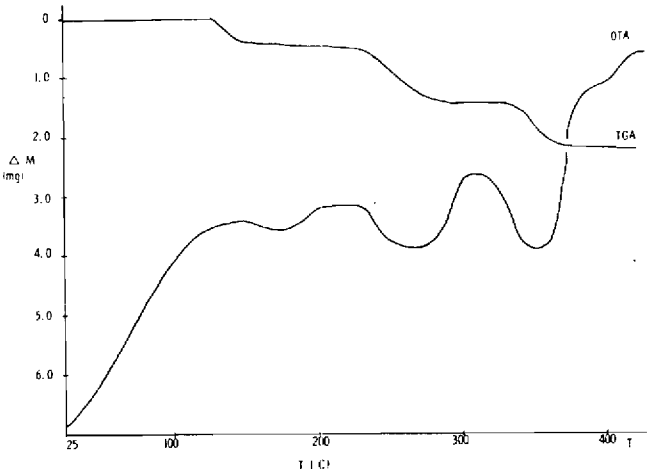


Figure 6. Dta-tga of K_2ZnH_4 under Ar.

composition steps at 242, 292, and 336°. No attempt was made to study the precise reactions involved in the decomposition steps. In the present work, the endothermal weight loss at 150° was found to be due to loss of solvent, since an X-ray powder diffraction pattern of a sample heated to 200° contained lines due only to K_2ZnH_4. The endothermal weight loss at 266° can be represented by the reaction shown in eq 16 since an X-ray powder pattern of a sample heated

$$K_2ZnH_4 \rightarrow 2KH + Zn + H_2 \quad (16)$$

to 300° showed lines due only to KH and zinc metal. Thus, the last endotherm can be represented by the reaction shown in eq 17.

$$2KH \rightarrow 2K + H_2 \quad (17)$$

KZn_3H_7. Reaction of a 1:3 mixture of KH and $(CH_3)_2Zn$ with AlH_3 in tetrahydrofuran gave a white solid with K:Zn:H ratio of 1:3:7; however, the X-ray powder diffraction pattern showed only lines for KZn_2H_5. Thus, the compound must be a 1:1 mixture of KZn_2H_5 and ZnH_2.

$KZnH_3$. The reaction of $KZn(CH_3)_2H$ with $LiAlH_4$ in

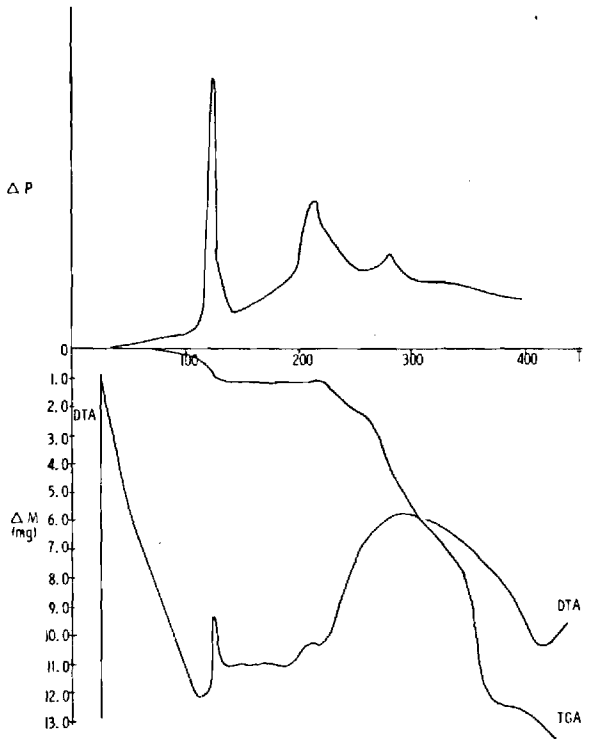


Figure 7. Vacuum dta-tga of $KZnH_3$.

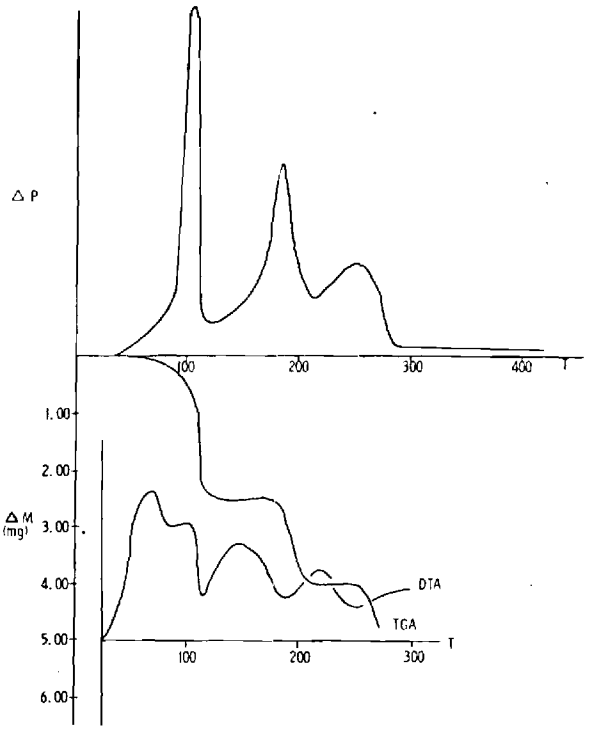


Figure 8. Vacuum dta-tga of $NaZnH_3$.

tetrahydrofuran gave $KZnH_3$ (no alkali metal exchange) in quantitative yield (eq 18). The X-ray powder diffraction

$$KZn(CH_3)_2H + LiAlH_4 \rightarrow KZnH_3 + LiAl(CH_3)_2H_2 \quad (18)$$

pattern of $KZnH_3$ (Table II) did not contain any lines due to KZn_2H_5, K_2ZnH_4, ZnH_2, or KH.

The vacuum dta-tga of $KZnH_3$ is shown in Figure 7. Three stages of noncondensable gas evolution were observed at 125, 213, and 280°. The weight losses accompanying the first and second stages of gas evolution were equivalent. The X-ray powder diffraction pattern of the solid left after the first gas evolution showed lines for K_2ZnH_4 and Zn only. The X-ray powder pattern of the solid left after the second gas evolution showed lines due to KH and Zn. These data lead to the following suggested decomposition pattern of $KZnH_3$. The weight losses during steps 1 and 2 should be equivalent. This is what was observed.

step 1: $KZnH_3 \rightarrow K_2ZnH_4 + Zn + H_2$

step 2: $K_2ZnH_4 \rightarrow 2KH + Zn + H_2$

step 3: $KH \rightarrow K + {}^1/_2H_2$

$NaZnH_3$. The reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in tetrahydrofuran gave $NaZnH_3$ (eq 19). The X-ray diffrac-

$$NaZn(CH_3)_2H + NaAlH_4 \rightarrow NaZnH_3 + NaAl(CH_3)_2H_2 \quad (19)$$

tion pattern (Table III) was identical with that reported by Shriver[10] in his preparation of $NaZnH_3$. [Shriver's preparation involved thermal decomposition of $NaZn_2(CH_3)_2H_3$ under vacuum to give $NaZnH_3$ and $(CH_3)_2Zn$]. Vacuum dta-tga analysis of $NaZnH_3$, shown in Figure 8, showed a strong exotherm at 72° and moderate endotherms at 104, 183, and 250°. The simultaneous weight loss curve showed inflections that correspond to equivalent weight losses at each of the endotherms and no weight loss at the exotherm. The first endotherm (104°) corresponds to the thermal decomposition of ZnH_2; therefore, the exotherm at 72° can be attributed to disproportionation of $NaZnH_3$ to Na_2ZnH_4 and Zn. This observation explains why $NaZnH_3$ turns

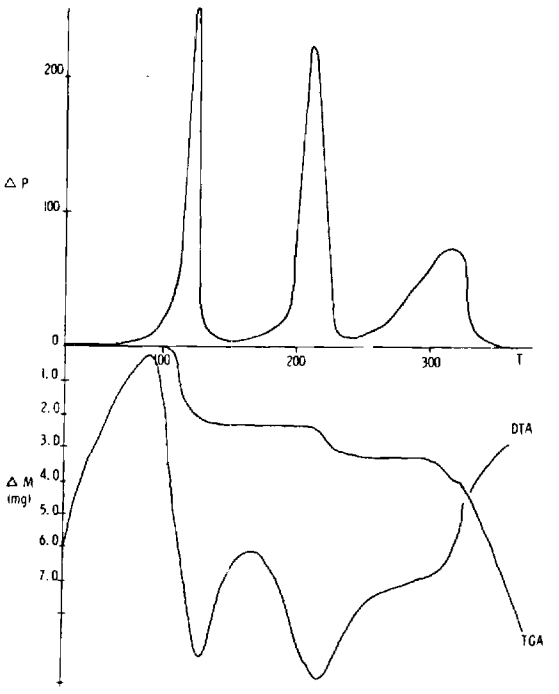


Figure 9. Vacuum dta-tga of $NaZn_2H_5$.

black on standing at room temperature (a phenomenon reported by Shriver[9] and observed by the authors). The endotherm at 183° corresponds to the decomposition of Na_2ZnH_4 and the endotherm at 250° corresponds to the decomposition of NaH. The dta-tga reported previously by us is different from the one reported here; however, the difference is probably due to the fact that the earlier dta-tga was run under argon at 1 atm of pressure, whereas the dta-tga reported here was carried out under vacuum. Thermal decomposition of $NaZnH_3$ is believed to proceed by the following series of steps.

step 1: $2NaZnH_3 \rightarrow Na_2ZnH_4 + ZnH_2$

step 2: $ZnH_2 \rightarrow Zn + H_2$

step 3: $Na_2ZnH_4 \rightarrow 2NaH + Zn + H_2$

step 4: $2NaH \rightarrow 2Na + H_2$

The reaction of $NaZn_2(CH_3)_4H$ with $NaAlH_4$ also yielded $NaZnH_3$. The X-ray powder diffraction pattern of $NaZnH_3$ prepared by this route is given in Table III. The mechanism by which $NaZnH_3$ was formed in this reaction is not understood at present.

$NaZn_2H_5$. In a manner similar to the reaction of $KZn(CH_3)_2H$ with AlH_3 which formed KZn_2H_5, AlH_3 was also found to react with $NaZn(CH_3)_2H$ to form $NaZn_2H_5$ (eq 20). The X-ray powder pattern of $NaZn_2H_5$ (Table III)

$$2NaZn(CH_3)_2H + 2AlH_3 \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \quad (20)$$

contained no lines due to NaH, ZnH_2, Na_2ZnH_4, or $NaZnH_3$. The infrared spectrum of the filtrate remaining after filtration of the solid $NaZn_2H_5$ showed a very broad band in the Al-H stretching region centered at 1610 cm^{-1}. In view of this spectrum and elemental analysis of the filtrate, the product in solution is believed to be a complex between Me_2AlH and $NaAlMe_2H_2$.

The vacuum dta-tga of $NaZn_2H_5$ is shown in Figure 9. Large evolutions of noncondensable gas occurred at 123, 210, and 315°. The ratio of the weight loss during the first gas evolution to that during the second and third ones was 3:1:1. The thermal effect for the first gas evolution was endothermal. This endotherm is believed to be due to disproportionation of $NaZn_2H_5$ to Na_2ZnH_4 and ZnH_2 with simultaneous decomposition of the ZnH_2. The thermal effects for the second and third gas evolutions were also endothermal. The second gas evolution is due to decomposition of Na_2ZnH_4 to NaH and ZnH_2 with simultaneous decomposition of ZnH_2. The third gas evolution is due to decomposition of NaH. The mechanism of decomposition, shown in the three steps below, is supported by X-ray powder diffraction data, taken after the first two stages of gas evolution. The X-ray powder pattern taken after the first step showed lines for Na_2ZnH_4 and Zn metal only. The X-ray powder pattern taken after the second step showed lines for NaH and Zn metal. More evidence is provided by the fact that the ratio of the weight losses in the three steps should be 3:1:1, which is what was observed.

step 1: $NaZn_2H_5 \rightarrow {}^1/_2Na_2ZnH_4 + {}^3/_2Zn + {}^3/_2H_2$

step 2: ${}^1/_2Na_2ZnH_4 \rightarrow NaH + {}^1/_2Zn + {}^1/_2H_2$

step 3: $NaH \rightarrow Na + {}^1/_2H_2$

Acknowledgment. We are indebted to the Office of Naval Research (Contract No. N000 14-67-A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

Registry No. LiH, 7580-67-8; (*sec*-$C_4H_9)_2Zn$, 7446-94-8; $LiAlH_4$, 16853-85-3; Li_2ZnH_4, 38829-84-4; $(CH_3)_2Zn$, 544-97-8; CH_3Li, 917-54-4; $LiZnH_3$, 38829-83-3; Li_3ZnH_5, 38887-62-6; KH, 7693-26-7; $KZn(CH_3)_2H$, 41202-98-6; AlH_3, 7784-21-6; KZn_2H_5, 37276-96-3; NaH, 7646-69-7; $NaAlH_4$, 13770-96-2; $NaZnH_3$, 34397-46-1; $NaZn_2H_5$, 39356-34-8.

[Reprinted from the Journal of the American Chemical Society, 95, 6485 (1973).]

Diethyl Ether Soluble Aluminum Hydride[1]

Sir:

We would like to report the preparation of diethyl ether soluble aluminum hydride prepared by three different reactions: (1) the reaction of lithium aluminum hydride and beryllium chloride, (2) the reaction of 100% H_2SO_4 with lithium aluminum hydride, and (3) the reaction of lithium aluminum hydride and zinc chloride. The yield in all three cases is quantitative.

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3 \quad (1)$$

$$2LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2AlH_3 \quad (2)$$

$$2LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2\,LiCl\downarrow + ZnH_2\downarrow + 2AlH_3 \quad (3)$$

Previous to this report soluble aluminum hydride could only be prepared in tetrahydrofuran. All attempts to prepare aluminum hydride in diethyl ether according to the method of Schlesinger (eq 4) resulted

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} LiCl\downarrow + 4AlH_3\downarrow \quad (4)$$

in significant precipitation of the aluminum hydride within 20 min after the rapid addition of reactants.[2,3]

To 20 mmol of $LiAlH_4$ in 150 ml of ether was added 10 mmol of $BeCl_2$. The solution was stirred for 2 hr and filtered. Analysis of the filtrate gave an Al:H:Li ratio of 1.0:2.97:0.002. No beryllium or chlorine was detected in the solution. Reversing the order of addition of the reactants yielded the same results. No precipitate of AlH_3 from solution was observed after 24 hr. The concentration of the solution dropped 4% in 1 week and 20% in 2 weeks. The infrared spectrum of the resulting solution[3] of AlH_3 (before precipitation) prepared by the Schlesinger method showed an Al–H stretching vibration at 1801 cm^{-1}. The AlH_3 which we have prepared has absorption bands at 1788 cm^{-1} owing to the Al–H stretching vibration and at 765 cm^{-1} owing to the Al–H deformation vibration.

Removal of the solvent under vacuum yields a white solid which was shown by elemental analysis to have the empirical formula of $AlH_3 \cdot 0.24(C_2H_5)_2O$. The X-ray powder diffraction pattern of this solid shows five main lines: 11.5 Å (s); 4.55 Å (m); 3.85 Å (m); 2.85 Å (m); and 2.32 Å (m). Bousquet, Choury, and Claudy,[4] have reported a powder pattern for $AlH_3 \cdot 0.25(C_2H_5)_2O$. Their lines match ours with the exception of the line at 3.85 Å.

DTA–TGA analysis of the solid AlH_3 etherate prepared from $LiAlH_4$ and $BeCl_2$ shows that evolution of ether begins at 50°. Evolution of hydrogen begins at 90° and is centered at 110°. Molecular association studies on a freshly prepared sample of AlH_3 in ether indicate that AlH_3 prepared from $LiAlH_4$ and $BeCl_2$ is monomeric at a concentration of 0.13–0.16 *m*.

The reduction of ketones was investigated in order to evaluate ether soluble AlH_3 as a stereoselective reducing agent. With 4-*tert*-butylcyclohexanone, AlH_3 in diethyl ether gave 46% axial alcohol, compared with 13% axial alcohol using AlH_3 in THF and 12% axial alcohol using $LiAlH_4$ in ether.

The preparation of soluble AlH_3 in diethyl ether provides an opportunity to prepare compounds that normally disproportionate in THF solvent. For example, we have prepared HBeCl by reaction of AlH_3 with $BeCl_2$ (eq 5). HBeCl was prepared unequivocally from

$$AlH_3 + BeCl_2 \longrightarrow HBeCl + H_2AlCl \quad (5)$$

BeH_2 and $BeCl_2$ in diethyl ether establishing the infrared bands for HBeCl at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl had disappeared in DBeCl. Molecular weight determination of HBeCl in ether shows the compound to be dimeric indicating that the BeH frequency at 1330 cm^{-1} is a bridge stretching mode.[5]

Exactly why stable ether solutions of AlH_3 are so easily prepared by the presently reported methods (eq 1–3), whereas all reports in the past claimed AlH_3 precipitates from ether, is not understood. We are, however, investigating this aspect further.[6]

Since MH_2 compounds of group II metals are insoluble in all organic solvents, it has been impossible to assign exact vibrational frequencies for the M–H band. It appears now that stable HMX compounds can be prepared from MX_2 and AlH_3 in ether, thus providing a means of obtaining stretching and deformation frequencies for M–H compounds. In this connection we are continuing our studies concerning reactions of AlH_3 in ether with groups I, II, and III metal halides.

(1) We are indebted to the Office of Naval Research (Contract No. N00014-67A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

(2) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 69, 1199 (1947).

(3) R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, 2, 650 (1963).

(4) J. Bousquet, J. J. Choury, and P. Claudy, *Bull. Soc. Chim. Fr.*, 3848 (1967).

(5) N. A. Bell and G. E. Coates, *J. Chem. Soc.*, 892 (1965).

(6) NOTE ADDED IN PROOF. We have just found that preparation of AlH_3 by the Schlesinger method also results in ether-soluble AlH_3 under comparable reaction conditions. We are presently investigating the effect of $LiAlH_4$ purity and lithium content in the product AlH_3 as sources of this unique behavior.

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Preparation of the First Complex Metal Hydride of Copper, $LiCuH_2$

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Summary

Reaction of $LiCu(CH_3)_2$ at low temperature with $LiAlH_4$ in diethyl ether results in the formation of a highly pyrophoric but stable solid whose analysis is consistent with the formula $LiCuH_2$.

Recently, considerable interest has been generated in copper chemistry, specifically in the area of synthetic applications involving lithium alkylcuprates[1] and copper hydride.[2,3] In view of the unusual chemistry of both of these reagents, we have been interested in the preparation of stable complex metal hydrides of copper in order to study there usefulness as reducing agents in organic chemistry.

Copper hydride prepared in ether is not stable at room temperature, decomposing with evolution of hydrogen to form a black solid.[4] Stable solutions of CuH in pyridine have been prepared by Dilts and Shriver[2] who have shown that the solubility of CuH is due to its complexation with the Lewis base. Stable complexes of CuH with triphenylphosphine have also been prepared by Churchill and co-workers.[3] The X-ray crystal structure determination showed the compound to be hexameric. This ability of CuH to undergo complex formation suggested to us that it should be possible to synthesize complex metal hydrides of copper. Our experience with complex metal hydrides of zinc (e.g., $LiZnH_3$, Li_2ZnH_4, etc.) suggest that complex metal hydrides of copper should be more stable than CuH itself.[5]

With this objective in mind we prepared a complex metal hydride of copper which is more stable than CuH by the reaction of lithium dimethylcuprate with lithium aluminum hydride in diethyl ether. To a slurry of 18 mmole CuI in 200 ml diethyl ether at -78° was added 36 mmole methyl lithium

$$CH_3Li + CuCl \rightarrow CH_3Cu + LiCl \quad (1)$$

$$CH_3Cu + CH_3Li \rightarrow LiCu(CH_3)_2 \quad (2)$$

$$LiCu(CH_3)_2 + LiAlH_4 \rightarrow LiCuH_2 + LiAl(CH_3)_2H \quad (3)$$

in ether. The solution was stirred for 1 hr at -78° at which time all the CuI had dissolved. To this was added 18 mmole of $LiAlH_4$ in ether. No precipitate formed at -78°; however, while warming the solution to room temperature, a yellow solid precipitated from solution. The reaction mixture was filtered and the yellow solid isolated as an ether slurry. This slurry gave the following analysis. Li:Cu:H:Al; 1.03:1.0:2.06:0.08. The infrared spectrum of the filtrate corresponded to that of $LiAlH_2(CH_3)_2$. DTA-TGA analysis of solid $LiCuH_2$ shows that decomposition takes place violently at 70°. No sharp lines, but rather two broad diffuse lines were observed in the X-ray powder pattern of the solid $LiCuH_2$. When stored as an ether slurry, $LiCuH_2$ is stable at room temperature for several days, unlike CuH alone (prepared in diethyl ether) which decomposes immediately upon warming to room temperature.[4] We have studied the preparation of this compound and other stoichiometric complex metal hydrides of copper, e.g., Li_3CuH_4, under a variety of conditions and in different solvents. We shall report on this study in more detail in the near future.

Reduction of isophorone with $LiCuH_2$ in ether yielded 3,5,5-trimethylcyclohex-2-ene-1-ol. Reduction of dihydroisophorone with $LiCuH_2$

in ether yielded 70% axial alcohol and 30% equatorial alcohol.

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2. J. A. Dilts and D. F. Shriver, J. Amer. Chem. Soc., 90, 5796 (1968).

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4. J. C. Warf and W. Feitkneckt, Helv. Chim. Acta, 33, 613 (1950).

5. J. J. Watkins and E. C. Ashby, J. C. S. Chem. Comm., 1972, 998.

Concerning the Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether

E. C. Ashby, P. Claudy and R. D.Schwartz

Abstract

The reaction of aluminum hydride with beryllium chloride in diethyl ether has been studied by infrared spectroscopy. The reaction proceeds according to the following equations.

$$BeCl_2 + AlH_3 \longrightarrow H_2AlCl + HBeCl$$

$$HBeCl + AlH_3 \rightleftharpoons H_2AlCl + BeH_2$$

Hydridoberyllium chloride was prepared unequivocally by the reaction of BeH_2 and $BeCl_2$ and shown to be the product of the above reaction. When AlH_3 is used in excess, BeH_2 precipitates from solution. The yield of BeH_2 depends on the amount of excess AlH_3 used. Hydridoberyllium chloride is stable to disproportionation and is dimeric in ether solvent. and Definitive beryllium-hydrogen stretching/deformation frequencies are reported.

Introduction

In a study of the reaction of lithium aluminum hydride with beryllium chloride, we[1] reported experimental results which could be explained by assuming an exchange between aluminum hydride and beryllium chloride to yield hydridoberyllium chloride and dihydridoaluminum chloride

$$AlH_3 + BeCl_2 \longrightarrow HBeCl + H_2AlCl \qquad (1)$$

(eq. 1). The suspected HBeCl formed in this reaction was soluble in ether

(1) E. C. Ashby, J. R. Sanders, P. Claudy and R. D. Schwartz, Inorg. Chem., in press.

as was the H_2AlCl. However, Dymova[2] has reported that the reaction of

(2) T. N. Dymova, M. S. Roshshina, S. Grazullne, V. A. Kuznetson, Dok. Akad. Nauk, SSR. 184, 1338 (1964) (English Translation).

lithium aluminum hydride and beryllium chloride in a 2:1 ratio yields $LiAl_2H_7$ and HBeCl which he reports to be insoluble in ether solvent.

$$2\ LiAlH_4 + BeCl_2 \longrightarrow HBeCl\downarrow + LiCl\downarrow + LiAl_2H_7 \qquad (2)$$

The preparation of $HBeX\cdot NR_3$ (where X = Cl, Br, I and NR_3 = N-methyl pyrrolidine and other tertiary amines) by several different methods has been claimed in a patent.[3]

(3) L. Sheperd (Ethyl Corp.) U.S. 3,483,219, Dec. 9, (1969).

We have undertaken to study the redistribution of AlH_3 with $BeCl_2$ in ether in order to establish (1) the true nature of the products of the reaction of $LiAlH_4$ and $BeCl_2$ in ether, (2) the physical properties of HBeCl, particularly the Be-H stretching and deformation frequencies and (3) the value of AlH_3 as a reagent for preparing HMX compounds by redistribution of AlH_3 in ether solvent with Groups II and III metal halides.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water or on the bench using typical Schlenk-tube techniques.[4]

(4) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 257 infrared spectrophotometer using NaCl liquid cells. Ebullioscopic molecular weight measurements were carried out as described previously.[5]

(5) F. W. Walker and E. C. Ashby, J. Chem. Ed., 45, 654 (1968).

Reagents. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Benzene (Fisher Certified reagent) was distilled over sodium aluminum hydride immediately prior to use. Anhydrous beryllium chloride was obtained from Columbia Organic Chemical Co. To a slurry of beryllium chloride in benzene cooled to 0°, was added excess diethyl ether (50% excess based on the bis etherate of beryllium chloride). The resulting solution was then filtered and the benzene was removed from the filtrate under vacuum. The resulting solid was then dissolved in ether. The resulting solution was then standardized by beryllium and chloride analysis. Ether solutions of anhydrous $AlCl_3$ (Fisher Certified reagent) were prepared in a manner similar to that of $BeCl_2$.

Preparation of Aluminum Hydride in Deithyl Fther. Lithium aluminum hydride was added to beryllium chloride in diethyl ether in a 2:1 ratio.[1] The resulting solution was then filtered. Analysis of the filtrate gave a Al:H:Li:Cl ratio of 1.00:3.02:.06:.01.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with Toepler pump. Aluminum analysis was carried out by titration with EDTA. Chloride was determined by potentiometric titration using Ag/glass electrodes. The sum 3 Al + 2 Be was

determined by adding excess NaF to the solution at pH = 7.8, and then back titrating to pH = 7.8 using standard hydrochloric acid.

Infrared Study of the Reaction of AlH_3 with $BeCl_2$ in Diethyl Ether. To 15 ml of AlH_3 in ether (0.07 M) in a 25 ml volumetric flask was added a volume of $BeCl_2$ in ether (0.225 M) calculated to give the desired AlH_3 to $BeCl_2$ ratio. The solution was then adjusted to the 25 ml mark and stirred. Ratios of 1:2, 1:1 and 2:1 AlH_3:$BeCl_2$ were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1. They showed no change after 24 hours.

When the $BeCl_2$ was added to the AlH_3 solution, a white precipitate formed immediately. This precipitate redissolved when the AlH_3: $BeCl_2$ ratio was 1:2 or 1:1. In order to identify the precipitate, 30 ml of $BeCl_2$ solution (0.225 M)was added to 90 ml of AlH_3 in ether (0.165 M). The reaction mixture was then filtered. Analysis of the solid obtained from the filtration gave the following Be:H:Cl ratios: 1.00:1.87:0.25. The amount of beryllium in the solid represented 6.5% of the total beryllium added.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ in Diethyl Ether. The choloroaluminum hydrides, H_2AlCl and $HAlCl_2$, were prepared by mixing AlH_3 and $AlCl_3$ in ether in the appropriate ratios. The reaction between AlH_3 and $AlCl_3$ has been discussed by a number of authors.[6,7,8] The

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(6) E. Wiberg, M. Schmidt, F. Natueforsch, 6b, 460 (1951).

(7) S. M. Arkhipov, V. I. Mikheeva, Zh. Neorg. Khim., 11, 2206 (1966).

(8) E. C. Ashby, J. Prather, J. Am. Chem. Soc., 88, 729 (1966).

infrared spectra of AlH_3, H_2AlCl and $HAlCl_2$ are reported in Figure 2.

Preparation of HBeCl from BeH_2 and $BeCl_2$ in Diethyl Ether. To 6.086 gm of $BeBr_2 \cdot 2Et_2O$ in 100 ml ether was added 35 ml of $LiAlH_4$ in ether (1.119 M). The solution was stirred overnight and then filtered. Analysis of the resulting solid gave a Be:H ratio of 1.00:1.90. To 6.80 mmoles of this solid product was added 25 ml of $BeCl_2$ in ether (0.2325 M). The solution was stirred overnight and filtered. Analysis of the filtrate gave a H:Be:Cl ratio of 0.92:1.00:1.08. The infrared spectrum of the solution vs. ether showed bands at 1330, 1050, 970, 908, 840, 840 (sh), 790 and 700 cm^{-1} (see Figure 3).

The compound DBeCl was prepared from BeD_2 and $BeCl_2$ in ether. Its infrared spectrum showed that the band at 1330 cm^{-1} in HBeCl shifted in DBeCl to 985 cm^{-1}. The band at 970 cm^{-1} in HBeCl disappeared in DBeCl. All the other bands in HBeCl were the same in DBeCl. Removal of the ether from the solution of HBeCl yielded an oil which was not characterized further. Ebullioscopic molecular weight determination of HBeCl in ether indicated that this compound is a dimer in the concentration range 0.1 to 0.3 molal.

Reaction of AlH_3 with $BeCl_2$ in Et_2O at 4:1 and 8:1 Ratios. To 50 ml of $BeCl_2$ in diethyl ether (.2067 M) was added 17 ml of $LiAlH_4$ in ether (1.156 M). The solution was stirred for 1 hr. and filtered. To the filtrate which was found to contain no lithium was added 25 ml of $BeCl_2$ in ether (0.2067 M) and the solution was stirred overnight. The solution was then filtered and the resulting solid gave a Be:H ratio of 1.00:1.90. This represented 34.8% of the original amount of beryllium.

In a similar experiment AlH_3 was allowed to react with $BeCl_2$ in

ether in a ratio of 8:1. In this case 56% of the original beryllium was isolated in the solid.

Results and Discussion

In our study of the reaction of lithium aluminum hydride with beryllium chloride in diethyl ether in 2:1 ratio, we found that the AlH_3 formed in this reaction is soluble in ether. When the above reaction is carried out in 1:1 ratio, a mixture of products was formed which was attributed to further reaction of AlH_3 with unreacted $BeCl_2$. In an effort to establish the nature of these products we decided to study the reaction of AlH_3 with $BeCl_2$ in ether in some detail.

Since hydrogen-halogen exchange in the AlH_3-$BeCl_2$ system would be expected to form hydridochloroalanes as well as HBeCl, it was decided that the hydridochloroalanes would have to be prepared first for infrared spectroscopic comparison purposes. Ether soluble alane was found to show bands in its infrared spectrum at 1788 and 770 cm^{-1}. When AlH_3 and $AlCl_3$ were mixed in a ratio of 2:1, H_2AlCl is produced. This compound has infrared bands at 1850, 1820 (sh), 780 and 725 cm^{-1}. The compound $HAlCl_2$ is produced where AlH_3 and $AlCl_3$ are allowed to react in 1:2 ratio. Its infrared spectrum shows bands at 1905, 1850 and 780 cm^{-1}.

$$2\ AlH_3 + AlCl_3 \rightarrow 3\ H_2AlCl \qquad (3)$$

$$AlH_3 + 2\ AlCl_3 \rightarrow 3\ HAlCl_2 \qquad (4)$$

When $BeCl_2$ is added to AlH_3 in ether in 2:1 ratio, a precipitate forms initially which redissolves as the $BeCl_2$ is added. When the addition is complete, the reaction solution is clear. The infrared spectrum

of the solution shows bands at 1850, 970, 905, 780, and 725 cm^{-1}. It is interesting that no bands characteristic of AlH_3 or $HAlCl_2$ are present. The bands at 1850, 780, and 725 cm^{-1} can be attributed to H_2AlCl. The bands at 970 and 905 cm^{-1} were found to correspond to the compound HBeCl prepared independently from BeH_2 and $BeCl_2$. At an AlH_3 to $BeCl_2$ ratio of 1:1, the infrared spectrum of the resulting solution is unchanged. These data indicate that as $BeCl_2$ is added to AlH_3, H_2AlCl and HBeCl are formed.

$$AlH_3 + BeCl_2 \longrightarrow H_2AlCl + HBeCl \qquad (5)$$

At an AlH_3:$BeCl_2$ ratio of 2:1, the infrared spectrum showed bands at 1850 (sh), 1788, 970, 905, 772, and 725 cm^{-1}. These data correspond to a mixture of AlH_3 and H_2AlCl. The bands at 970 cm^{-1} and 905 cm^{-1} are again attributed to HBeCl. A small amount of solid precipitated from the reaction mixture. The solid was found to be BeH_2 and represented 6% of the total beryllium added. At AlH_3:$BeCl_2$ ratios of 4:1 and 8:1 larger amounts of solid were isolated. This solid proved to be BeH_2 in yields of 34.8% and 56%, respectively. Alane was also found to reduce HBeCl in ether to BeH_2 in 63% yield (based on HBeCl) at an AlH_3:HBeCl ratio of 2:1.

$$2\,AlH_3 + HBeCl \rightleftharpoons BeH_2 \downarrow + H_2AlCl + AlH_3 \qquad (6)$$

The compound HBeCl was prepared independently by the redistribution of BeH_2 and $BeCl_2$ in ether. The infrared spectrum of HBeCl in ether showed bands at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The

$$BeH_2 + BeCl_2 \rightarrow 2\,HBeCl \qquad (7)$$

infrared spectrum of DBeCl showed that the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl disappeared in DBeCl. This gives a $\nu_H:\nu_D$ ratio of 1.35. Molecular weight determination of HBeCl in ether indicates that the compound is associated with an i value of 2.17 at 0.1 to 0.3 molal.

Coates and Roberts[9] isolated the complex $Be_2H_4 \cdot TMED$ which has a

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(9) G. E. Coates and P. D. Roberts, J. Chem. Soc., A, 1969, 1008.

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sharp doublet in the infrared spectrum at 1787 and 1807 cm^{-1}. They attribute these bands to terminal Be-H stretching vibrations. We find no bands in this region for HBeCl. Bell and Coates[10] have reported the

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(10) N. A. Bell and G. E. Coates, J. Chem. Soc., 1965, 692.

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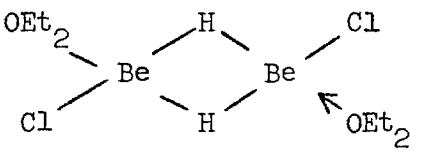
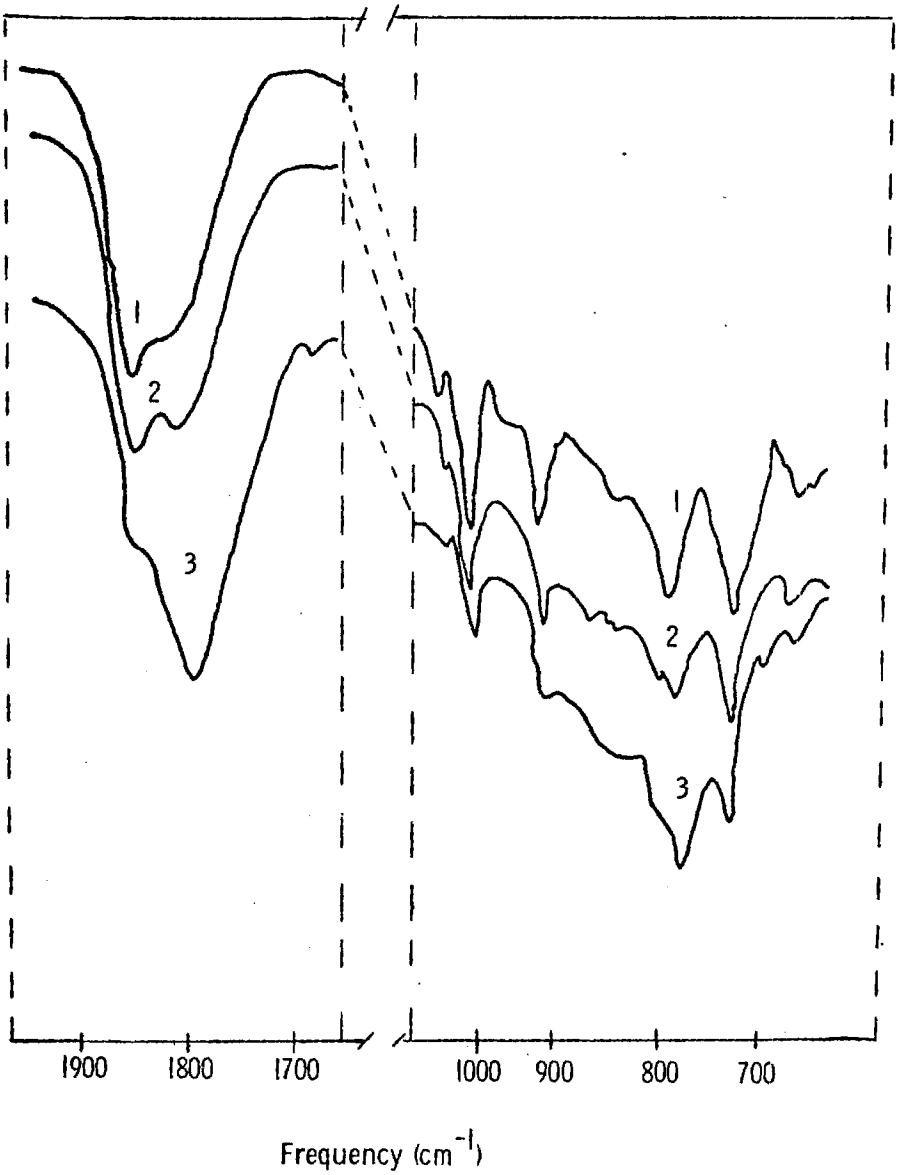
compounds $[CH_3BeH \cdot N(CH_3)_3]_2$ and $[C_2H_5BeH \cdot N(CH_3)_3]_2$ which are dimers in benzene. These compounds exhibit strong absorption at 1333-1344 cm^{-1} (in cyclohexane) which is attributed to the Be-H-Be bridge. In the deuterated compounds, the 1344 cm^{-1} band of $[CH_3BeH \cdot N(CH_3)_3]_2$ shifted to 1020 cm^{-1}. We therefore conclude that HBeCl is associated through Be-H-Be bridge bonds.



Acknowledgement. We acknowledge with gratitude support of this work by the Office of Naval Research.

Figure I. Infrared study of the reaction of AlH_3 with $BeCl_2$ in diethyl ether in (1) 1:2, (2) 1:1 and (3) 2:1 ratio.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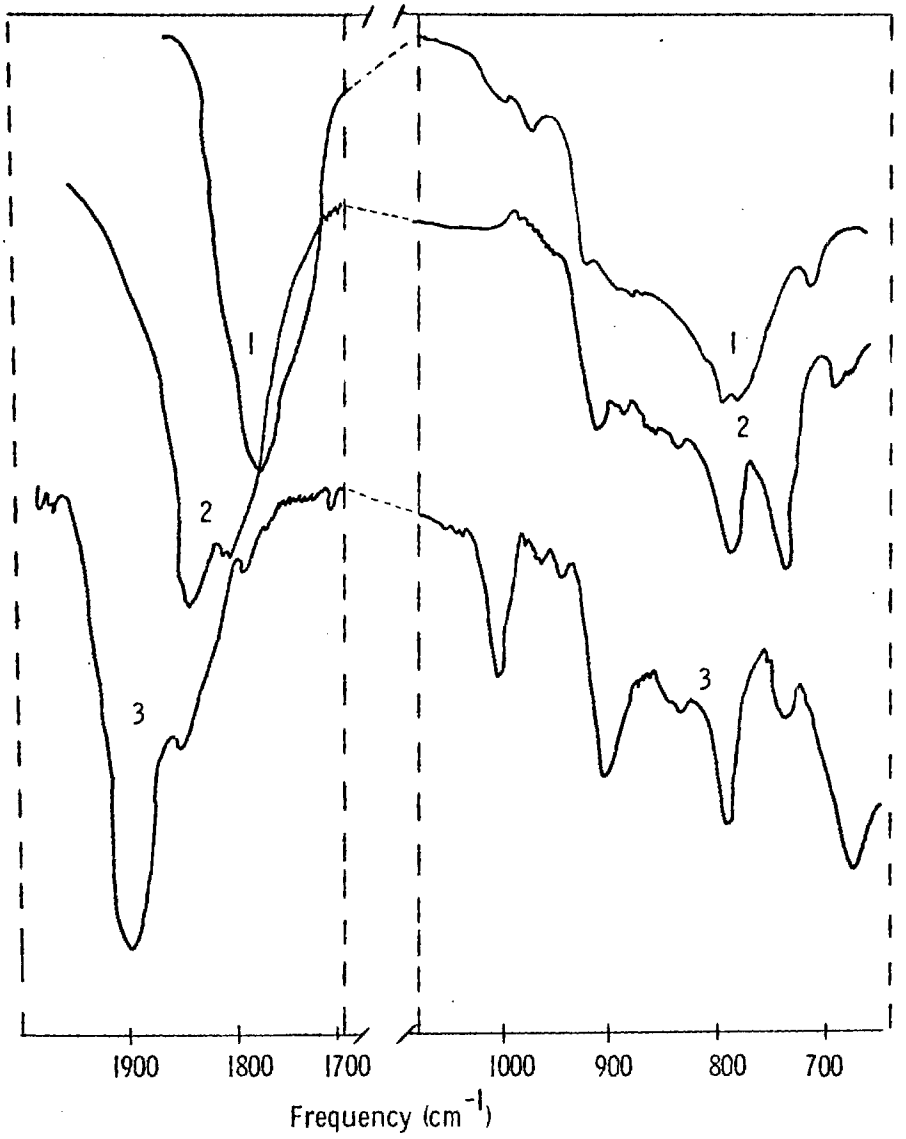
Frequency (cm⁻¹)

Figure 2. Infrared study of the reactions of AlH_3 with $AlCl_3$ in diethyl ether in (1) 1:0, (2) 2:1 and (3) 1:2 ratio.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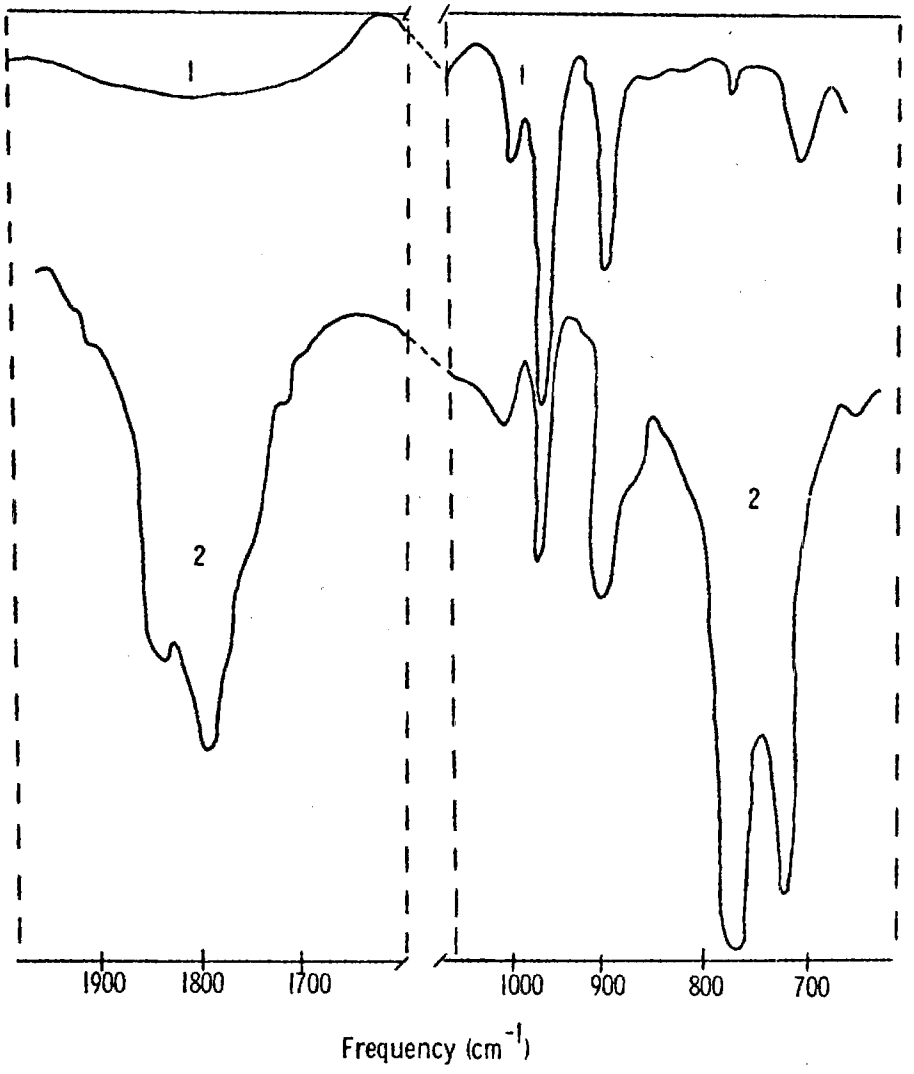
Frequency (cm^{-1})

Figure 3. Infrared study of the reaction of (1) BeH_2 with $BeCl_2$ in 1:1 ratio in diethyl ether and (2) AlH_3 with $BeCl_2$ in 1:1 ratio in diethyl ether.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Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Georgia Institute of Technology	non-classified
	2b. GROUP

REPORT TITLE

Complex Metal Hydrides.
High Energy Fuel Components for Solid Propellant Rocket Motors.

1. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Annual Report (March 1, 1973 - December 31, 1973)

5. AUTHOR(S) *(First name, middle initial, last name)*

Eugene C. Ashby

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
February 15, 1974	151	103

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
N00014-67-A-0159-005	
b. PROJECT NO.	
c. NA	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

During the fifth contract period work has continued on the preparation and structure elucidation of simple and complex metal hydrides of the main group elements. Three papers have appeared in the literature (two in Inorganic Chemistry and one in the Journal of the American Chemical Society and two papers are "in press", describing work carried out during the past year on this project. These papers are contained in the Appendix of this report. Projects completed during the past year are (1) a study concerning methods of preparation of diethyl ether soluble aluminum hydride (2) a study describing the preparation of complex metal hydrides of copper (3) a study concerning redistribution reactions of ether soluble aluminum hydride with Groups I and II A and B metal halides (4) a study concerning the desolvation of aluminum hydride and (5) a study concerning the mechanisms of preparation and reactions of compounds of the type $MZn_x(CH_3)_{2x}H$.

Security Classification

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
omplex Metal Hydrides						
igh Energy Fuels						
rganometallic Compounds						
igh Energy Binders						
urning Rate Accelerators						
olid Rocket Propellants						

D FORM 1 NOV 65 1473 (BACK)

N 0101-807-6821

Security Classification

A-31409

Annual Report

to the

Office of Naval Research

"Complex Metal Hydrides. High Energy Fuel Components for Solid Propellant Rocket Motors."

E. C. Ashby, Principal Investigator

Georgia Institute of Technology, Atlanta, Georgia 30332

January 1, 1974 - December 31, 1974

This Research was Sponsored by the Office of Naval Research

under Contract No. N00014-67-A-0519-005AD and

ONR Contract Authority No. NR 093-050/7-11-69(473)

Table of Contents

Manuscripts Published Since the Last Report Period

Abstract

The preparation of two new hydrides, $Mg(ZnH_3)_2$ and $MgZnH_4$ are reported by the reaction of $Mg[Zn(CH_3)_3]_2$ and $MgZn(CH_3)_4$ respectively with $LiAlH_4$ in diethyl ether solvent. The intermediate, $Mg[Zn(CH_3)_3]_2$, was prepared from $LiZn(CH_3)_3$ and $MgBr_2$ in 2:1 ratio and $MgZn(CH_3)_4$ was prepared from $Li_2Zn(CH_3)_4$ and $MgBr_2$ in 1:1 ratio.

The reactions of $LiAlH_4$ with "ate" complexes of beryllium ($Li_nBe_mR_{2m+n}$) were studied. So far Li_2BeH_4 and Li_3BeH_5 have been prepared and characterized. A detailed variable temperature nmr study of all possible "ate" complexes ($LiCH_3$:$(CH_3)_2Be$ ratio = 1:1, 2:1, 3:1 and 1:2) has been carried out in an attempt to determine the nature of the "ate" complex in solution before reduction with $LiAlH_4$.

A detailed variable temperature nmr study of $(CH_3)_2Zn$, $LiZn(CH_3)_2H$, $LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4H$ and $LiZn_2(CH_3)_4AlH_4$ has been carried out in an attempt to determine the structure and solution integrity of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$.

Four projects have been completed and the results submitted for publication in "Inorganic Chemistry Journal". The projects are entitled, "Concerning the Existence of Complexes of $LiAlH_4$ and AlH_3 in Ether Solvents and in the Solid State," "The Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc. I. The reaction of $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with Aluminum Hydride," "Reactions of Alkali Metal Hydrides with Magnesium Alkyls. Preparation of $MMgR_2H$ and MMg_2R_4H Compounds" and "Reactions of Aluminum Hydride with Groups I and II A and B Metal Halides."

Three manuscripts representing completed work have appeared in the literature. Two manuscripts have appeared in Inorganic Chemistry, "Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether," and "Reaction of Alkali Metal Hydrides with Zinc Halides in Tetrahydrofuran. A Convenient and Economic Preparation of Zinc Hydride." One manuscript has appeared in Journal of the Chemical Society D (Chemical Communications) entitled, "Preparation of the First Stable Complex Metal Hydride of Copper."

List of Manuscripts in Press and Published Since the Last Report Period

In Press

(1) E.C. Ashby and John Watkins, "Concerning the Existence of Complexes of $LiAlH_4$ and AlH_3 in Ether Solvents and in the Solid State," Inorganic Chemistry, (submitted April 2, 1974, accepted for publication October 31, 1974, to be published in March 1975.)

(2) E.C. Ashby and H. Prasad, "Reactions of Aluminum Hydride with Groups I and II A and B Metal Halides," Inorganic Chemistry, (submitted July 16, 1974, accepted for publication February 3, 1975, to be published in June 1975).

(3) E.C. Ashby and John J. Watkins, "The Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc. The Reaction of $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with Aluminum Hydride," Inorganic Chemistry, (submitted October 11, 1974).

(4) "Reactions of Alkali Metal Hydrides with Magnesium Alkyls. Preparation of $MMgR_2H$ and MMg_2R_4H Compounds," Inorganic Chemistry, (submitted for publication February 17, 1975).

Published

(1) E.C. Ashby, P. Claudy and R.D. Schwartz, "Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether," Inorg. Chem., 13, 192 (1974).

(2) John J. Watkins and E.C. Ashby, "Reaction of Alkali Metal Hydrides with Zinc Halides in Tetrahydrofuran. A Convenient and Economical Preparation of Zinc Hydride," Inorg. Chem., 13, 2350 (1974).

(3) E.C. Ashby, T. Korenowski and R.D. Schwartz, "Preparation of the First Stable Complex Metal Hydride of Copper, $LiCuH_2$", J.C.S., Chem. Comm., 157 (1974).

Preparation of $Mg(ZnH_3)_2$ and $MgZnH_4$

E.C. Ashby and K.C. Nainan

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

ABSTRACT

The reaction of CH_3Li with $(CH_3)_2Zn$ in 1:1 and 2:1 molar ratio in diethylether solvent produced $LiZn(CH_3)_3$ and $Li_2Zn(CH_3)_4$ respectively. These 'ate' complexes reacted metathetically with magnesium-bromide in diethylether to produce ether soluble magnesium tri- and tetramethyl zincates, $Mg[Zn(CH_3)_3]_2$ and $MgZn(CH_3)_4$, which on reduction with $LiAlH_4$ gives ether insoluble magnesium tri- and tetrahydridozincates, $Mg(ZnH_3)_2$ and $MgZnH_4$. All the reactions proceed in diethyl ether at room temperature in high yield. All intermediates were characterized by elemental analysis and ir spectroscopy and the hydride products were characterized by elemental analysis, DTA-TGA and X-ray powder diffraction analysis.

Introduction

Recently, a number of lithium, sodium and potassium "hydridozincates" have been reported.[1] From our study of complex ternary metal hydrides

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(1) D.J. Hurd, J. Org. Chem., 13, 711 (1948); (b) L.M. Seitz and J.L. Brown, J. Amer. Chem. Soc., 88, 4140 (1966); (c) E.C. Ashby and John Watkins, J. Chem. Soc., D., 998 (1972); (d) E.C. Ashby and John J. Watkins, Inorg. Chem., 12, 2493 (1973).

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of the type, $M_nM'H_{2+n}$ (where n = 1,2 or 3), we have found that one of the important factors that determines the stability of the hydrides to decomposition, $M_nM'H_{2+n} \rightarrow n(MH) + M'H_2$, is the electronegativity

difference between M and M'. Evidence so far indicates that M must be more electropositive than M' in the preparation of a stable ternary hydride. Based on this principle we are now in the process of preparing and investigating the chemistry and uses of various metal hydride systems, $M_nM'H_{2+n}$ in which M is other than an alkali metal. In this paper, we are reporting two new complex metal hydrides derived from magnesium and zinc.

Experimental Section

Reactions were performed under nitrogen at the bench[2] or in a dry box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice-acetone to remove solvent vapours.[3]

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(2) D.F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, N.Y., 1969.

(3) E.C. Ashby and R.D. Schwartz, J. Chem. Ed., 51, 65 (1974).

Filtrations and other manipulations were carried out in the drybox. All compounds were dried to a constant weight on a high vacuum line.

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as Nujol (dried over sodium and stored in drybox) mulls between CsI plates and solutions were run in matched 0.10-mm path length KBr cells. X-ray powder data were obtained on a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered CuKα radiation. Samples were sealed (in drybox) in 0.5-mm capillaries and exposed to x-rays for 4-6 hours. d spacings were read on a precalibrated scale equipped with viewing apparatus and the intensities of the lines were

visually estimated. DTA-TGA were obtained under vacuum, static pressure or argon gas flow. Details of the instrument (Mettler thermoanalyzer II) and procedure are given elsewhere.[1c]

Materials. Dimethylzinc was prepared by a modification of Noller's general procedure for preparation of dialkyl zinc compounds.[4] Ether

(4) C.R. Noller, Org. Syn., 12, 86 (1932).

solutions of magnesium bromide and lithium aluminum hydride (ventron, Metal Hydride Division) were prepared by previously published methods.[5,6]

(5) R.G. Beach and E.C. Ashby, Inorg. Chem., 10, 1888 (1971).

(6) E.C. Ashby, R.D. Schwartz and B.D. James, Inorg. Chem., 9, 325 (1970).

Methyllithium in ether solution was obtained from Matheson Coleman and Bell and stored at -20° until ready to use. The reactants were standardized by analysis and transferred volumetrically. Diethyl ether was distilled fresh from $LiAlH_4$ just before use.

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexometric titration with EDTA. Zinc and magnesium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Zinc in the presence of magnesium and aluminum was determined by masking with ammonium fluoride. Aluminum and zinc in the presence of

magnesium could be determined by standard EDTA titration (Ph = 4.0) using dithizone indicator. Analysis for halides was carried out using Volhard procedure.

$Mg(ZnH_3)_2$. In a 200 ml 3-necked round bottom flask containing 10 ml of 0.892 molar (8.92 mmols) dimethylzinc in diethylether was added under nitrogen with stirring 5.30 ml of 1.682 molar (8.92 mmols) methyllithium in ether. After stirring the solution at room temperature for about forty minutes, 36 ml of 0.124 molar (4.46 mmols) magnesium bromide in diethyl ether was added and stirred for about three hours. When an ether solution of lithium aluminum hydride, 16 ml of 0.835 molar (13.36 mmols), was added slowly to the stirred reaction mixture, a white precipitate rapidly formed which was stirred for an additional one hour at room temperature. The white solid was filtered under vacuum using a medium frit filter funnel and washed with about 300 ml of freshly distilled diethyl ether in small portions. The resulting solid was vacuum dried (.05 mm) for 1 1/2 hours at room temperature and weighed 0.880 g (95% yield). Anal. Calcd for $Mg(ZnH_3)_2$, $0.732(C_2H_5)_2O$: Mg, 11.29; Zn, 60.76; H, 2.81; $(C_2H_5)_2O$, 25.17; Found: Mg, 10.98; Zn, 59.23; H, 2.79; $(C_2H_5)_2O$, 24.53. The molar ratio of Mg:Zn:H was 1.00:2.01:6.12.

Magnesium Tetrahydridozincate. The procedure of this experiment was similar to the previous one. Dimethyl zinc (7.93 mmols) in diethylether was added to 15.86 mmols of methyllithium in ether and stirred for about an hour at room temperature, followed by addition of 7.93 mmols of magnesium bromide ether solution. The resulting solution was stirred for 3 hours and then 15.86 mmols of ether solution of lithium aluminum hydride was added. A white solid was immediately formed which was stirred for an additional hour

before it was filtered, and washed with 300 ml of dry ether. The compound was vacuum dried (10^{-5} mm) for 17 hours and weighed 0.551 g. Anal. Calcd for $MgZnH_4 \cdot 0.1(C_2H_5)_2O$. Mg, 24.12; Zn, 64.88; H, 4.00, $(C_2H_5)_2O$, 6.98; Found, Mg, 22.84; Zn, 62.27; H, 3.80; $(C_2H_5)_2O$, 6.65. The molar ratio of Mg:Zn:H was 1.00:1.01:3.98.

Results and Discussion

Magnesium trihydridozincate [$Mg(ZnH_3)_2$] was prepared by the following series of reactions.

$$CH_3Li + (CH_3)_2Zn \longrightarrow LiZn(CH_3)_3 \qquad (1)$$

$$2\ LiZn(CH_3)_3 + MgBr_2 \longrightarrow Mg[Zn(CH_3)_3]_2 + 2\ LiBr \qquad (2)$$

$$Mg[Zn(CH_3)_3]_2 + 3\ LiAlH_4 \longrightarrow Mg(ZnH_3)_2 + 3\ LiAl(CH_3)_2H_2 \qquad (3)$$

When an ether solution of CH_3Li was added to an ether solution of $(CH_3)_2Zn$ a clear colorless solution resulted. To this solution containing $LiZn(CH_3)_3$ was added $MgBr_2$ which resulted in the formation of a clear and colorless solution containing $Mg[Zn(CH_3)_3]_2$ and LiBr. When $LiAlH_4$ was added to this solution, an immediate white precipitate of $Mg(ZnH_3)_2$ resulted.

Magnesium tetrahydridozincate ($MgZnH_4$) was prepared according to a series of reactions similar to that used for the preparation of $Mg(ZnH_3)_2$.

$$2\ CH_3Li + (CH_3)_2Zn \longrightarrow Li_2Zn(CH_3)_4 \qquad (4)$$

$$Li_2Zn(CH_3)_4 + MgBr_2 \longrightarrow MgZn(CH_3)_4 + 2LiBr \qquad (5)$$

$$MgZn(CH_3)_4 + 2\ LiAlH_4 \longrightarrow MgZnH_4 + 2\ LiAl(CH_3)_2H_2 \qquad (6)$$

The intermediates $Li_2Zn(CH_3)_4$ and $MgZn(CH_3)_4$ were soluble in ether whereas the final product $MgZnH_4$ was insoluble.

Both $Mg(ZnH_3)_2$ and $MgZnH_4$ are white solids, which slowly turn black on standing at room temperature, but could be stored in dry ice for an indefinite period of time. They are very sensitive to air and moisture, and sparingly soluble in ether. Infrared analysis (Nujol mull) of both compounds showed two broad bands, one at 400-650 cm^{-1} and one at 1200-1900 cm^{-1}. No nmr data could be obtained due to the poor solubility of the compounds.

Magnesium trihydridozincate [$Mg(ZnH_3)_2$] gave a characteristic X-ray powder diffraction pattern which did not contain lines due to MgH_2 or ZnH_2. The predominant interplanar spacing and the corresponding relative intensities (estimated visually) are: d = 6.0 (W); 4.50 (V.S.); 3.85 (M); 3.25 (S); 2.80 (m.s.); 1.98 (m); 2.5 (V.W.); Magnesium tetrahydridozincate ($MgZnH_4$) did not give any X-ray powder diffraction pattern, probably due to the amorphous nature of the compound.

The thermal decomposition (dta-tga) of these two metal hydrides is not straightforward, probably due to the presence of the solvating ether molecules. It has been shown that unsolvated alkali metal borohydride (BH_4^-) and aluminohydride (AlH^-_4) thermally decompose in an understandable manner whereas solvated magnesium and calcium analogs decompose irratically and irreproducibly due to the formation of alkoxy species during heating.[6] A similar situation is observed in the thermal decomposition of $Mg(ZnH_3)_2$ and $MgZnH_4$, although straightforward dta-tga patterns[1d] in the case of $LiZnH_3$ and Li_2ZnH_4 were observed.

The vacuum dta-tga of $Mg(ZnH_3)_2$ $0.480(C_2H_5)_2O$ contained non-condensable gases near 100° (8.4% wt. loss, exothermic), 160°

(0.5% wt. loss, exo), 200° (1.2% wt. loss, exo) and near 315° (exo) the gas evolution is followed by a sudden and large decrease in wt. loss due to evaporation or sublimation of some of the products of thermal decomposition. The vacuum dta-tga of $MgZnH_4$ $0.1(C_2H_5)_2O$, was more complicated than that of $Mg(ZnH_3)_2$. The evolution of non-condensable gas at different temperatures with corresponding % wt. loss and thermicity are as follows: 85°, 2.94%, exo; 100°, 1.40%, exo; 130°, 0.42%, exo; 215°, 0.84%, exo; 270°, 0.98%, exo; 325°, 0.84%, endo. From these present data no definite conclusion could be drawn. One explanation that might be given for the observed irratic thermal behavior is the probable formation of alkoxy species during heating. Some additional work is now underway in order to determine the correct path of thermal decomposition of these metal hydrides when prepared as unsolvated compounds. As observed from dta-tga, in general

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(6) J.A. Dilts and E.C. Ashby, Inorg. Chem., 11, 1230 (1972).

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the thermal stability of magnesium compounds is lower than that of the corresponding alkali metal (Li, Na and K) compounds,[1d] and this is probably due to the lower electropositivity of magnesium compared to lithium, sodium and potassium.

It has been shown by low temperature nmr studies[1b] that in diethylether substitution of one unit of methyllithium from tetrameric methyllithium by one molecule of dimethylzinc forms $Li_3Zn(CH_3)_5$ (eq. 7).

$$(LiCH_3)_4 + (CH_3)_2Zn \longrightarrow Li_3Zn(CH_3)_5 + CH_3Li \qquad (7)$$

It has been shown that $LiZnH_3$ is conveniently prepared by the reduction of $LiZn(CH_3)_3$ with $LiAlH_4$. The $LiZn(CH_3)_3$ was formed in ether solution by substitution of two methyllithium units in the methyllithium tetramer by two molecules of dimethylzinc when they were mixed in 1:1 molar ratio (eq. 8,9).

$$1/2(LiCH_3)_4 + 2Zn(CH_3)_2 \longrightarrow 2LiZn(CH_3)_3 \qquad (8)$$

$$LiZn(CH_3)_3 + 3/2\ LiAlH_4 \longrightarrow LiZnH_3 + 3/2\ LiAl(CH_3)_2H_2 \qquad (9)$$

$LiZn(CH_3)_3$ is one of the intermediates in the preparation of $Mg(ZnH_3)_3$. $Li_2Zn(CH_3)_4$ which is a precursor to $MgZnH_4$ was first prepared by Hurd in 1948[1a], characterized both by nmr[1b] and x-ray crystallography.[7]

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(7) E. Weiss and R. Wolfrum, Chem. Ber., 101, 35 (1968).

The reduction of this compound by $LiAlH_4$ was shown to give Li_2ZnH_4.[1d] It was thought that since magnesium is more electropositive than zinc, formation of $Mg[Zn(CH_3)_3]_2$ and $MgZn(CH_3)_4$ from the metathetic reaction of $LiZn(CH_3)_3$ and $Li_2Zn(CH_3)_4$ with $MgBr_2$ followed by subsequent reduction with $LiAlH_4$ would give $Mg(ZnH_3)_2$ and $MgZnH_4$ respectively.

Comparison of powder patterns of MgH_2 (only strong lines cited) d = 3.19 VS, 2.49 VS, 1.59 S, 1.67 S,[8] and ZnH_2, 4.23 S, 2.82 S, 2.60 S,

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(8) E.C. Ashby, R. Kovar and R. Arnott, J. Amer. Chem. Soc., 92, 2182 (1970).

2.46 S[1d,9] with that of $Mg(ZnH_3)_2$, 4.50 VS, 3.25 S, 2.80 ms, indicates

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(9) John J. Watkins and E.C. Ashby, Inorg. Chem. 13, 2350 (1974).

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that it is not a mixture of MgH_2 and ZnH_2. Due to the failure to get a powder pattern for $MgZnH_4$, the question whether it is a true compound or an equimolar mixture of MgH_2 and ZnH_2 is not fully answered. We are now taking steps to study the dta-tga of freshly prepared MgH_2 and ZnH_2 and their mixture in order to get more information about the true nature of $MgZnH_4$.

ALKALI METAL "ATE" COMPLEXES AND COMPLEX METAL HYDRIDES OF BERYLLIUM

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ABSTRACT

The reactions of lithium aluminum hydride with "ate" complexes of beryllium ($Li_nBe_mR_{2m+n}$) in ether solvents were investigated as a possible route to complex metal hydrides of beryllium. Both the 1:1 and 2:1 complexes of methyllithium and dimethylberyllium [$LiBe(CH_3)_3$ and $Li_2Be(CH_3)_4$] yielded Li_2BeH_4 when allowed to react with $LiAlH_4$ in diethyl ether. Li_3BeH_5 was obtained by a similar reaction of methyllithium and dimethylberyllium in 3:1 molar ratio followed by the reduction of the "ate" complex [$Li_3Be(CH_3)_5$] with $LiAlH_4$ in diethyl ether. The 1:2 complex of methyllithium and dimethylberyllium [$LiBe_2(CH_3)_5$] yielded a compound of indefinite composition. Proton nmr spectra of diethyl ether solutions of methyllithium and dimethylberyllium in 1:1, 2:1, 3:1 and 1:2 molar ratio have been obtained over a wide temperature range. The spectra show that there is rapid exchange of methyl groups between methyllithium and complex. Evidence for the existence of more than one complex at equilibrium is discussed.

INTRODUCTION

Recently we have reported the synthesis of complex metal hydrides of zinc[1] and magnesium.[2] The preparation of these compounds involves

(1) E.C. Ashby and John J. Watkins, Inorg. Chem., 12, 2493 (1973).

(2) E.C. Ashby, Suresh C. Srivastava and John J. Watkins, Inorg. Chem. (in press).

the reduction of an "ate" complex ($M_nM'_mR_{2m+n}$) with either $LiAlH_4$ or AlH_3.

$$CH_3Li + (CH_3)_2M \longrightarrow \underset{\downarrow LiAlH_4}{LiM(CH_3)_3} \xrightarrow{CH_3Li} \underset{\downarrow LiAlH_4}{Li_2M(CH_3)_4} \xrightarrow{CH_3Li} \underset{\downarrow LiAlH_4}{Li_3M(CH_3)_5} \qquad (1)$$

$$\underset{\text{(where M = Zn or Mg)}}{CH_3Li + 2\,(CH_3)_2M \longrightarrow LiM_2(CH_3)_5 \xrightarrow{LiAlH_4} LiM_2H_5} \qquad (2)$$

In 1968, Coates and Bell[3] reported the preparation of Li_2BeH_4 by the

(3) N.A. Bell and G.E. Coates, J. Chem. Soc., (A), 628 (1968).

reaction of beryllium chloride and $Li(C_2H_5)_2BeH$. Attempts were also made to prepare other complex metal hydrides of beryllium, e.g. $LiBeH_3$; however no evidence was found to support the existence of this compound.

Recently Seitz and coworkers[4,5] studied Lithium-7 and Proton nmr

(4) Larry M. Seitz and Theodore L. Brown, J. Amer. Chem. Soc., 88, 4140 (1966).

(5) Larry M. Seitz and B.F. Little, J. Organometal. Chem., 18, 227 (1969).

spectra of methyllithium with $(CH_3)_2Mg$, $(CH_3)_2Zn$ and $(CH_3)_2Cd$ in diethyl ether. The spectra show that complexes of the type $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ (where M = Mg, Zn, or Cd) are formed in solution. No attempts were made to isolate these complexes in the pure form. No evidence was available for or against the formation of a 1:1 complex. In our earlier work,[6,7] we studied the system methyllithium-dimethyl-

(6) E.C. Ashby and R.C. Arnott, J. Organometal. Chem., 21, p.29 (1970).

(7) E.C. Ashby and R.C. Arnott, unpublished results.

magnesium in diethyl ether by high resolution infrared spectroscopy and found in general that at any given concentration there are several "ate" complex species in equilibrium and at no time does a single complex exist in solution.

In view of our recent preparation of complex metal hydrides of zinc and magnesium by the reaction of $LiAlH_4$ with the corresponding "ate" complexes, we decided to carry out a similar study involving the reactions of $LiAlH_4$ and "ate" complexes of beryllium. In this paper, we describe the preparation and characterization of Li_2BeH_4 and Li_3BeH_5. Also the system $CH_3Li/(CH_3)_2Be$ in diethyl ether was studied by Proton nmr and high resolution infrared

spectroscopy in order to define the composition of the "ate" complex in solution prior to reaction with $LiAlH_4$.

EXPERIMENTAL SECTION

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture[8]

(8) E.C. Ashby and R.D. Schwartz, J. Chem. Ed., 51, 65 (1974).

or on the bench top using typical Schlenk-tube techniques.[9]

(9) D.H. Shriver, The Manipulation of Air-Sensitive Compounds. McGraw-Hill, New York, 1969.

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solid samples were obtained as mulls in nujol between CsI plates. Solutions were run in matched 0.10 mm path length KBr cells. X-ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered $CuK\alpha$ radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 8 - 10 hrs. d - Spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA-TGA data were obtained under vacuum with a modified Mettler Thermoanalyzer II.

Proton spectra were obtained at 60 MHz using varian A60 spectrometer. The low temperatures were obtained using the standard low-temperature

accessories supplied by Varian Associates.

Analytical Procedures: Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analysis was carried out by complexiметric titration with EDTA. Beryllium was determined by adding excess sodium flouride to the solution at pH 7.8 and then back-titrating to pH 7.8 using standard hydrochloric acid. Lithium analysis was carried out by flame photometry. Analysis for chloride was carried out using a modified Volhard procedure. Analysis for carbon-bonded and oxygen-bonded metals was carried out by the Watson and Eastham[10] method using 2,2'-biquinoline and phenolphthalein indicators.

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(10) S.C. Watson and J.F. Eastham, J. Organometal. Chem., 9, 165 (1967).

Materials: Diethyl ether (Fisher anhydrous ether) was distilled over $LiAlH_4$ immediately prior to use. Benzene (Fisher certified reagent) was distilled over sodium aluminum hydride. Lithium aluminum hydride was obtained as a gray powder from Ventron, Metal hydrides Division. Solutions of $LiAlH_4$ in diethyl ether was prepared by stirring the solid hydride for 24 hours with freshly distilled solvent, followed by filtration in a glove box to yield a clear, colorless solution. Anhydrous beryllium chloride was obtained from Alfa Inorganics. A solution of beryllium chloride in diethyl ether was prepared by adding excess diethyl ether (50% excess based on the bis-etherate of beryllium chloride) to a slurry of $BeCl_2$ in benzene cooled at 0°.[11] Ether solutions

(11) E.C. Ashby, P. Claudy, and R.D. Schwartz, Inorg. Chem., 13, 192 (1974).

of $BeBr_2$ were prepared as previously reported.[12] Methyllithium was

(12) E.C. Ashby, R. Sanders, and J. Carter, Chem. Comm., 997 (1967).

obtained as a 5.4% solution in ether from Foote Mineral Company and stored at -20° until ready to use. Sodium hydride was prepared by hydrogenation of metallic sodium in benzene at 4000 psi for 24 hours. A slurry of sodium hydride in diethyl ether was prepared in the usual manner. Lithium hydride was prepared by hydrogenolysis of tert-butyllithium in pentane at 4000 psi for 24 hours.

Preparation of Dimethylberyllium in Diethyl Ether. A solution of methyllithium in ether was added slowly to a solution of beryllium chloride in ether in 2:1 molar ratio. Lithium chloride precipitated immediately and was separated by filtration. The filtrate was evaporated to dryness under vacuum at room temperature and dimethylberyllium (white solid) was purified by sublimation under vacuum (0.05 mm of Hg) at 110°. A solution of dimethylberyllium in ether was then prepared by dissolving the purified compound in ether. Analysis showed a $Be:CH_4$ ratio of 1.00:1.98.

Preparation of $(n\text{-}C_4H_9)_2Be$ in Diethyl Ether. 20 mmole of $n\text{-}C_4H_9Li$ in hexane was added slowly with stirring to a cold solution (0°) of $BeCl_2$ (10 mmole) in diethyl ether. Lithium chloride precipitated and was

filtered. The filtrate was concentrated and analyzed for beryllium and n-butyl group in the usual manner (Be:C_4H_{10} = 1.0:1.92).

Infrared Study of the Reaction of $(CH_3)_2Be$ with CH_3Li in Diethyl Ether. To 2 ml of $(CH_3)_2Be$ (0.623M) in a 10 ml volumetric flask was added a volume of CH_3Li in ether (1.586M) calculated to give the desired $(CH_3)_2Be$ to CH_3Li ratio. The solution was then adjusted to the 10 ml mark and stirred. $(CH_3)_2Be$:CH_3Li ratios of 1:1, 1:2, 1:3 and 2:1 were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1.

Proton NMR Study of the Reaction of $(CH_3)_2Be$ with CH_3Li in Diethyl Ether. Ether solutions of CH_3Li and $(CH_3)_2Be$ were mixed in the appropriate molar ratios to form $Li_nBe_m(CH_3)_{2m+n}$ (where n = 1,2,3 when m = 1, and n = 0.5 when m = 2). The solutions were transferred into 5 mm nmr tubes under nitrogen and stored in dry ice.

Reactions Involving $(CH_3)_2Be$ with CH_3Li. (a) Reaction of $LiAlH_4$ with $LiBe(CH_3)_3$ in Diethyl Ether. Attempted Preparation of $LiBeH_3$. Methyllithium (5 mmole) in diethyl ether was added to 5 mmole of dimethylberyllium in diethyl ether. The resulting solution was stirred at room temperature for one hour; then 5 mmole of $LiAlH_4$ in diethyl ether was added. A white precipitate appeared immediately. This mixture was stirred at room temperature for another hour and filtered. The white solid was dried at room temperature under vacuum and analyzed. Anal. Calcd for $LiBeH_3$: Li, 36.56; Be, 47.49; H, 15.94. Found: Li, 46.83; Be, 28.39; H, 12.76. The molar ratio of Li:Be:H was 2.08:1.00:4.01. The filtrate contained only aluminum and a trace of beryllium and lithium. The infrared spectrum

of the filtrate showed no Al-H stretching vibrations, but instead was about identical to the spectrum observed for $(CH_3)_3Al$. The X-ray powder diffraction pattern of the solid product contained lines due to Li_2BeH_4 only.

(b) Reaction of $LiAlH_4$ with $Li_2Be(CH_3)_4$ in Diethyl Ether. Preparation of Li_2BeH_4. Dimethylberyllium (20 mmole) in diethyl ether was added to 40 mmole of methyllithium in diethyl ether. The resulting solution was stirred for one hour at room temperature, followed by addition of 40 mmole of $LiAlH_4$ in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred for an additional one hour at room temperature, filtered, and dried under vacuum. Anal. calcd for $Li_2BeH_4 \cdot 0.047\ Et_2O$: Li, 45.65; Be, 29.64; H, 13.24. Found: Li, 46.82; Be, 25.58; H, 13.04. The molar ratio of Li:Be:H in the solid was 1.10: 0.517:2.110. The X-ray powder diffraction pattern, given in Table 1 was almost identical with the pattern reported earlier for Li_2BeH_4.[3]

(c) Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ in Diethyl Ether. Preparation of Li_3BeH_5. Methyllithium (42 mmole) in diethyl ether was added to 14 mmole of dimethylberyllium in diethyl ether. The resulting solution was stirred for one hour at room temperature, followed by addition of 35 mmole of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. The mixture was stirred for an additional hour at room temperature and filtered. The resulting white solid was then dried at room temperature under vacuum and analyzed. Anal. Calcd for $Li_3BeH_5 \cdot 0.23\ Et_2O$: Li, 40.09; Be, 17.35; H, 9.70. Found: Li, 38.14; Be, 18.07; H, 10.40. The molar ratio of Li:Be:H was 2.73:1.00:5.17. The amount of Li_3BeH_5

recovered was 100% of the theoretical value. The X-ray powder diffraction data are given in Table 1. Infrared analysis of the solid (Nujol mull) showed a broad strong band at 1400 - 1800 cm^{-1} (centered at 1600 cm^{-1}).

(d) Reaction of $LiAlH_4$ with $LiBe_2(CH_3)_5$ in Diethyl Ether. Attempted Preparation of $LiBe_2H_5$. Methyllithium (10 mmole) in diethyl ether was added to 20 mmole of dimethylberyllium in diethyl ether. The resulting solution was stirred for one hour, followed by addition of 17.5 mmole of $LiAlH_4$ in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred overnight at room temperature and then filtered. The white solid was then dried at room temperature under vacuum. The X-ray powder diffraction data are given in Table 1. Anal. calcd. for $LiBe_2H_5$: Li, 23.12; Be, 60.07; H, 16.79. Found: Li, 31.11; Be, 31.14; H, 11.61. The molar ratio of Li:Be:H was 1.16:0.907:3.00.

(e) Reaction of NaH with $(n\text{-}C_4H_9)_2Be$ in Diethyl Ether. Attempted Preparation of $NaBe(n\text{-}C_4H_9)_2H$. A slurry of sodium hydride (10 mmole) in diethyl ether was added to 10 mmole $(n\text{-}C_4H_9)_2Be$ in diethyl ether. The resulting mixture was stirred for 48 hours at room temperature and then filtered. An analysis of the filtrate showed Be:H in the ratio of 0.976:0.309 and the analysis of the white residue showed it to be unreacted sodium hydride.

(f) Reaction of $LiAlH_4$ with $BeBr_2$ in Diethyl Ether. Preparation of BeH_2. $LiAlH_4$ (14 mmole) solution in diethyl ether was added to 7 mmole $BeBr_2$ solution in diethyl ether and the mixture stirred for one hour at room temperature. The resulting white solid was filtered, washed with ether several times and dried at room temperature under vacuum. Anal. calcd. for $BeH_2 \cdot 0.21\ Et_2O$: Be, 33.88; H, 7.58. Found: Be, 34.54; H, 7.25. The molar ratio of Be:H was 0.53:1.00. The X-ray powder diffraction data are given in Table 1.

RESULTS AND DISCUSSION

Reactions Involving $(CH_3)_2Be$ and CH_3Li.

(a) Reaction of $LiAlH_4$ with $LiBe(CH_3)_3$ in Diethyl Ether. Attempted Preparation of $LiBeH_3$. The reaction of $(CH_3)_2Be$ with CH_3Li in diethyl ether yields a clear solution. The infrared spectrum of the resultant solution is recorded in Figure 1. Although no assignment has been made for M - C stretching vibrations, the absence of the 483 cm^{-1} band characteristic of methyllithium and the absence of the weak bands at 528 cm^{-1} and 472 cm^{-1} characteristic of dimethylberyllium, indicates the formation of a complex involving methyllithium and dimethylberyllium. The infrared spectrum of the solution shows two medium strong bands at 500 cm^{-1} and 400 cm^{-1} and a weak band at 450 cm^{-1}.

The proton nmr spectrum of the resulting "ate" complex in diethyl ether at room temperature is shown in Figure 2. At room temperature the proton chemical shifts of methyllithium and dimethylberyllium are 3.08 and 2.28 ppm, respectively, upfield from the center of the ether triplet. The proton spectrum of methyllithium-dimethylberyllium complex consists of a single sharp resonance at room temperature which implies either formation of a compound with only one type of methyl group or rapid exchange involving different species in solution. At low temperature (-96°) the exchange is slowed such that a multiplet structure occurs, as shown in Figure 3. The resonance peak at 2.23 ppm may be assigned to the methyl protons of the 1:1 complex, whereas the resonance peak at 2.65 ppm may be assigned to the methyl protons of the complex $Li_2Be(CH_3)_4$. The presence of the broad peak at 2.45 ppm is not well understood; however, it may be due to some kind of impurity which

could not be removed from the starting materials although considerable effort was made in this direction. The occurrence of this peak at low temperature has also been noted by Seitz and Little[6] while studying the methyllithium-dimethylcadmium system. It appears therefore, that at room temperature there is a rapid exchange between 2:1 and 1:1 complexes of methyllithium and dimethylberyllium giving a single sharp resonance and at low temperature this exchange is slowed to the extent that $LiBe(CH_3)_3$ and $Li_2Be(CH_3)_4$ exhibit individual methyl signals. It is clear that $LiBe(CH_3)_3$ is by far the most predominant species in solution; however, it is in equilibrium with $Li_2Be(CH_3)_4$ at room temperature.

The reaction of $LiAlH_4$ and $LiBe(CH_3)_3$ gave a solid which was shown to be Li_2BeH_4 instead of $LiBeH_3$. The infrared spectrum of the filtrate showed no bands due to Al-H stretching vibrations between 1900 - 1700 cm^{-1}; however, it did exhibit a spectrum almost identical to $(CH_3)_3Al$. The infrared spectrum of the white solid (in Nujol mull) contained broad absorptions centered at 1600 cm^{-1}. The X-ray powder diffraction pattern showed only lines for Li_2BeH_4 (Table 1). The route by which Li_2BeH_4 is formed from $LiBe(CH_3)_3$ and $LiAlH_4$ is not clear but probably takes place according to eqs. 3 and 4.

$$LiBe(CH_3)_3 + LiAlH_4 \longrightarrow Li_2Be(CH_3)_3H + AlH_3 \qquad (3)$$

$$Li_2Be(CH_3)_3H + AlH_3 \longrightarrow Li_2BeH_4 + Al(CH_3)_3 \qquad (4)$$

The vacuum tga shown in Figure 7 contained one very broad peak at 330°. This observation in addition to the pressure differential

curve peaking at 330° is indicative of the evolution of a noncondensable gas (H_2) and represents the only weight loss or gas evolution up to 500°. The thermal effect (dta) of this gas evolution is a small endotherm (330°) which is preceeded by another small endotherm at 270° indicative of a structural change not involving a weight loss or gas evolution. The weight loss at 330° (8%) corresponds to the loss of one mole of hydrogen present in Li_2BeH_4. Thus, the decomposition takes place according to eqs. 5 and 6 with Li_2BeH_4 dissociating to LiH and BeH_2 at 270° (no

$$Li_2BeH_4 \longrightarrow 2\,LiH + BeH_2 \quad \text{(endotherm, 270°)} \tag{5}$$

$$BeH_2 \longrightarrow Be + H_2 \quad \text{(endotherm, 330°)} \tag{6}$$

weight loss) followed by decomposition of the BeH_2 at 330°.

(b) Reaction of $LiAlH_4$ with $Li_2Be(CH_3)_4$ in Diethyl Ether. Preparation of Li_2BeH_4. The reaction of CH_3Li with $(CH_3)_2Be$ in 2:1 molar ratio also yields a clear solution. The infrared spectrum of the resultant solution shown in Figure 1 is identical with the infrared spectrum of the complex obtained before except that the band at 500 cm^{-1} is masked by the strong band of methyllithium at 483 cm^{-1}. The proton nmr spectrum of $Li_2Be(CH_3)_4$ in diethyl ether at room temperature is shown in Figure 2. At room temperature the proton spectrum consists of a single sharp resonance peak which again implies either a single compound or a rapid exchange among different species in solution. The low temperature (-96°) proton spectrum (Figure 4) can be interpreted in terms of an equilibrium mixture of

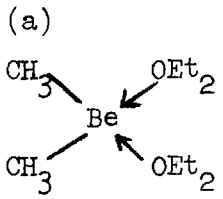
1:1, 2:1, and 3:1 complexes of methyllithium and dimethylberyllium.

$$1/4(CH_3Li)_4 + (CH_3)_2Be \longrightarrow LiBe(CH_3)_3 \quad (7)$$

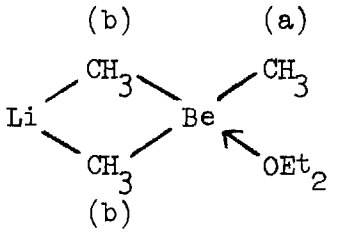
$$LiBe(CH_3)_3 + 1/4(CH_3Li)_4 \rightleftharpoons Li_2Be(CH_3)_4 \quad (8)$$

$$Li_2Be(CH_3)_4 + 1/4(CH_3Li)_4 \rightleftharpoons Li_3Be(CH_3)_5 \quad (9)$$

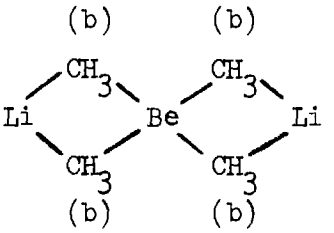
The methyl group (a) bonded directly to the beryllium atom in $(CH_3)_2Br\cdot OEt$ should be similar to one of the methyl groups in $LiBe(CH_3)_3\cdot OEt_2$ and $Li_3Be(CH_3)_5$. On the other hand the methyl group (b) bridged to Li and Be(Li-CH_3-Be) should be similar to the methyl group (b) in $Li_2Be(CH_3)_4$ and $Li_3Be(CH_3)_3$. Furthermore, the methyl group (c) bridged only to Li(Li-CH_3-Li) should be similar to the methyl group in $(CH_3Li)_4$ and $Li_3Be(CH_3)_5$ designated (c).



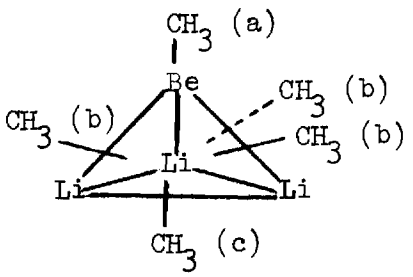
$[(CH_3)_2Be\cdot 2OEt_2]$



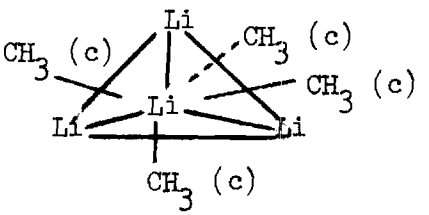
$[LiBe(CH_3)_3\cdot OEt_2]$



$[Li_2Be(CH_3)_4]$



$[Li_3Be(CH_3)_5]$



$[(CH_3Li)_4]$

The resonance furthest downfield is assigned to the methyl group (a) attached only to beryllium since $(CH_3)_2Be \cdot 2OEt_2$ absorbs in the region. The methyl group (c) has been assigned to the absorption furthest upfield because this methyl group is attached only to Li and therefore should resemble $(CH_3Li)_4$ which absorbs the furthest upfield. The methyl group (b) bonded to lithium and beryllium atoms should exhibit a chemical shift in between $(CH_3)_2Be \cdot OEt_2$ and $(CH_3Li)_4$. Using these ideas, the assignment of the resonance peaks can be made to substantiate the existence of the above equilibrium. (7-9)

The amount of each complex, namely, $LiBe(CH_3)_3$, $Li_2Be(CH_3)_4$ and $Li_3Be(CH_3)_5$ at equilibrium can be calculated by measuring the areas of each peak and taking into consideration the fact that each peak may be either due to methyl protons of only one specie or due to methyl protons of different species present in solution. For example, the resonance peak furthest downfield may be due to both of the methyl groups of $(CH_3)_2Be \cdot 2OEt_2$ as well as due to the methyl group bonded to the beryllium atom in $Li_3Be(CH_3)_5$. Similarly, the resonance peak observed for the 2:1 complex, $Li_2Be(CH_3)_4$, may also be due to the three methyl groups which are bonded to both lithium and beryllium atoms in $Li_3Be(CH_3)_5$. The resonance peak furthest upfield may only be due to the methyl group bonded to the three lithium atoms in the complex, $Li_3Be(CH_3)_5$ or to the presence of methyl lithium. It has been found from the measured areas (Table II) that $LiBe(CH_3)_3$, $Li_2Be(CH_3)_4$ and $Li_3Be(CH_3)_5$ exist in 1:1:1 molar ratio in solution at -96° when CH_3Li and $(CH_3)_2Be$ are admixed in 2:1 ratio.

The reaction of $LiAlH_4$ and ate complex mixture produced on reacting

CH_3Li and $(CH_3)_2Be$ in 2:1 ratio yielded a white solid of empirical formula Li_2BeH_4. The infrared spectrum of the white solid contained a broad absorption band centered on 1600 cm^{-1}. The X-ray powder diffraction pattern showed it to be Li_2BeH_4 (Table 1). The vacuum dta-tga of this compound was identical with the one discussed earlier. The major weight loss (7.7%) occurred at 330° corresponding to one mole of hydrogen.

(c) Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ in Diethyl Ether. Preparation of Li_3BeH_5. The infrared spectrum of the solution obtained by stirring a solution of CH_3Li with $(CH_3)_2Be$ in diethyl ether in 3:1 molar ratio is recorded in Figure 1. The infrared spectrum of the solution shows two medium strong bands at 405 cm^{-1} and 335 cm^{-1} which are tentatively assigned to Be-C stretching vibrations. The strong band at 480 cm^{-1} is assigned to the Li-C stretching vibrations. The proton spectrum of the same solution consists of a single sharp resonance at room temperature. This implies either the presence of a single compound or a rapid exchange between different species in solution. At low temperature a multiplet structures occurs, as shown in Figure 5. The assignment of these resonance peaks are made as before describing the system as an equilibrium of the following type:

$$1/4(CH_3Li)_4 + Li_2Be(CH_3)_4 \rightleftharpoons Li_3Be(CH_3)_5 \qquad (10)$$

In order to establish the stoichiometry of these complexes at equilibrium the areas of all absorptions in the low-temperature proton spectra were measured. A calculation of the relative peak intensities shows $Li_3Be(CH_3)_5$

to be major species in solution with ~ 10% dissociation to CH_3Li and $Li_2Be(CH_3)_4$, (Table 2).

Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ produced an insoluble white compound which exhibited the empirical formula Li_3BeH_5. The infrared spectrum of the solid showed a broad absorption band centered on 1600 cm^{-1}. The X-ray powder diffraction pattern showed it to be a new compound and not a physical mixture of LiH and Li_2BeH_4. The vacuum dta-tga of this compound (Figure 8) showed a weight loss (1.21%) at 218° and another weight loss (4.71%) at 300°; the total weight loss being 5.92% which is quite in agreement with the theoretical value (5.78%) calculated for the loss of one mole of hydrogen. Although this total weight loss due to evolution of hydrogen gas leads us to suggest the following steps of decomposition, the weight loss in two stages is somewhat puzzling.

Step I	$Li_3BeH_5 \longrightarrow Li_2BeH_5 + LiH$
Step II	$Li_2BeH_4 \longrightarrow 2LiH + BeH_2$
Step III	$BeH_2 \longrightarrow Be + H_2$

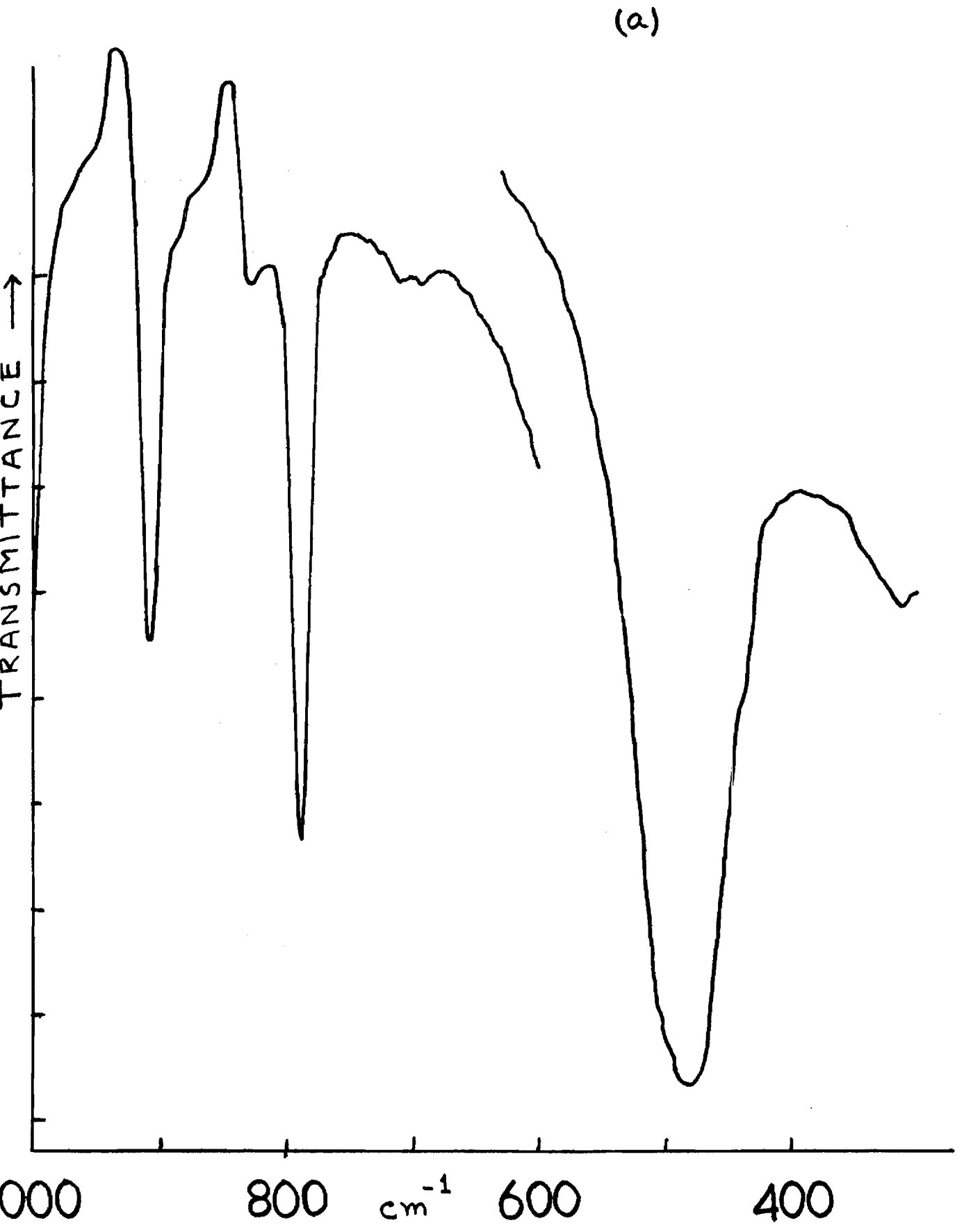
(d) Reaction of $LiAlH_4$ with $LiBe_2(CH_3)_5$ in Diethyl Ether. $LiBe_2H_5$. The infrared spectrum of the resultant mixture obtained after stirring CH_3Li with $(CH_3)_2Be$ in 1:2 molar ratio is identical with the infrared spectrum of the so called complex $LiBe(CH_3)_3$. The proton nmr spectrum of the solution consists of a single sharp resonance at room temperature as well as at low temperature (-96°) indicating a single compound or very rapid exchange of methyl groups between the complex $[LiBe(CH_3)_3]$ and dimethylberyllium. The reaction of $LiAlH_4$ with the 1:2 CH_3Li:$(CH_3)_2Be$ solution resulted in a solid of indefinite analysis. The X-ray powder

diffraction of the solid gave very weak lines similar to Li_2BeH_4, but with different intensities. It appears that the compound is a physical mixture of Li_2BeH_4 and BeH_2.

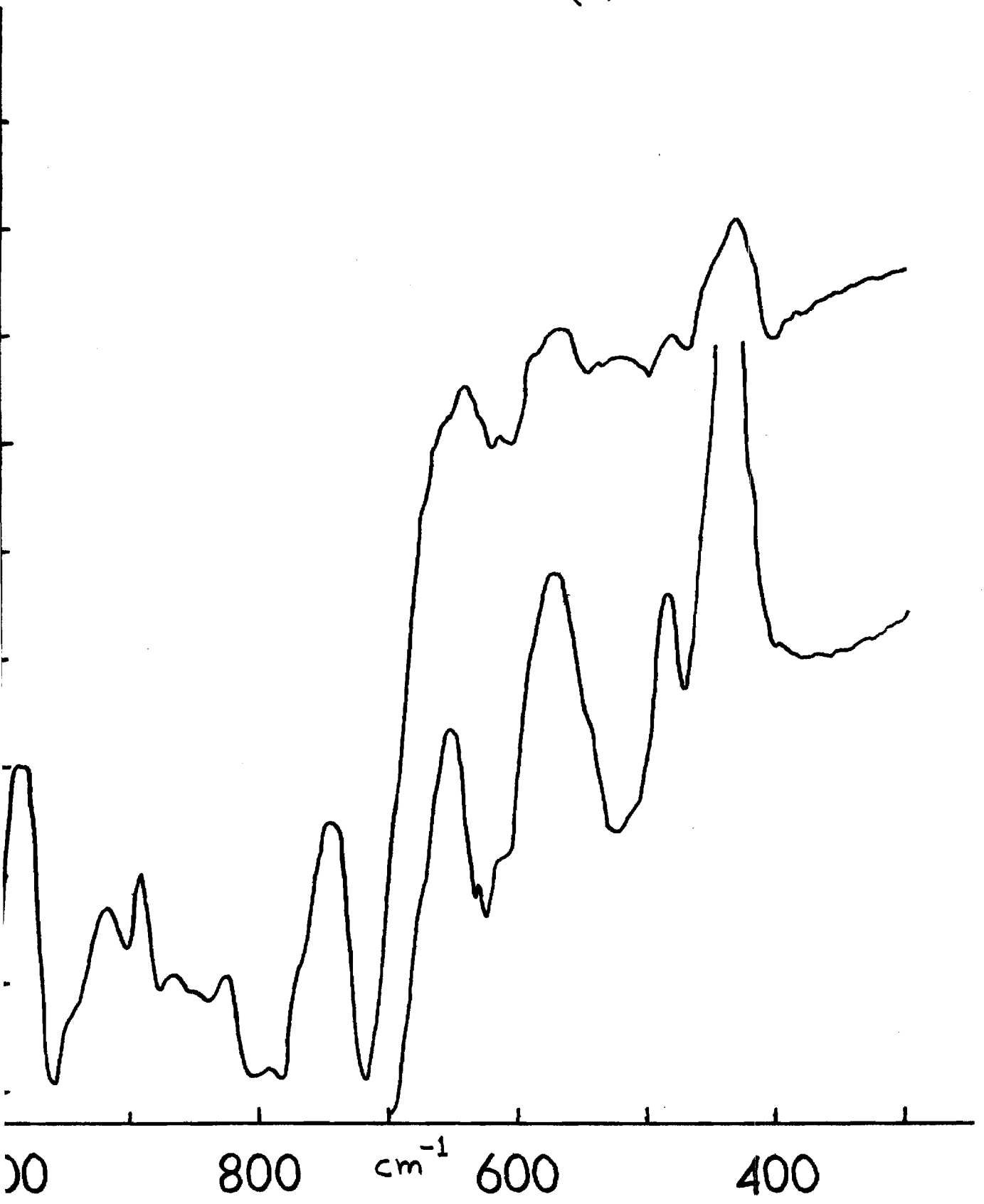
A potential route to complex metal hydrides of beryllium of the type $Na_nBe_mH_{2n+m}$ and $KnBe_mH_{2n+m}$ involves the reaction of NaH or KH with $(CH_3)_2Be$ followed by reaction of the resulting complex with $LiAlH_4$. Attempts to prepare $KBe(CH_3)_2H$ and $NaBe(s\text{-}C_4H_9)_2H$ in diethylether resulted in incomplete reaction between potassium or sodium hydride with corresponding dialkylberyllium compounds.

ACKNOWLEDGEMENT: We would like to acknowledge the financial support of the Office of Naval Research under Contract No. N 00014-67-A-0519-005 AD and ONR Contract Authority No. NR 093-050/7-11-69(473).

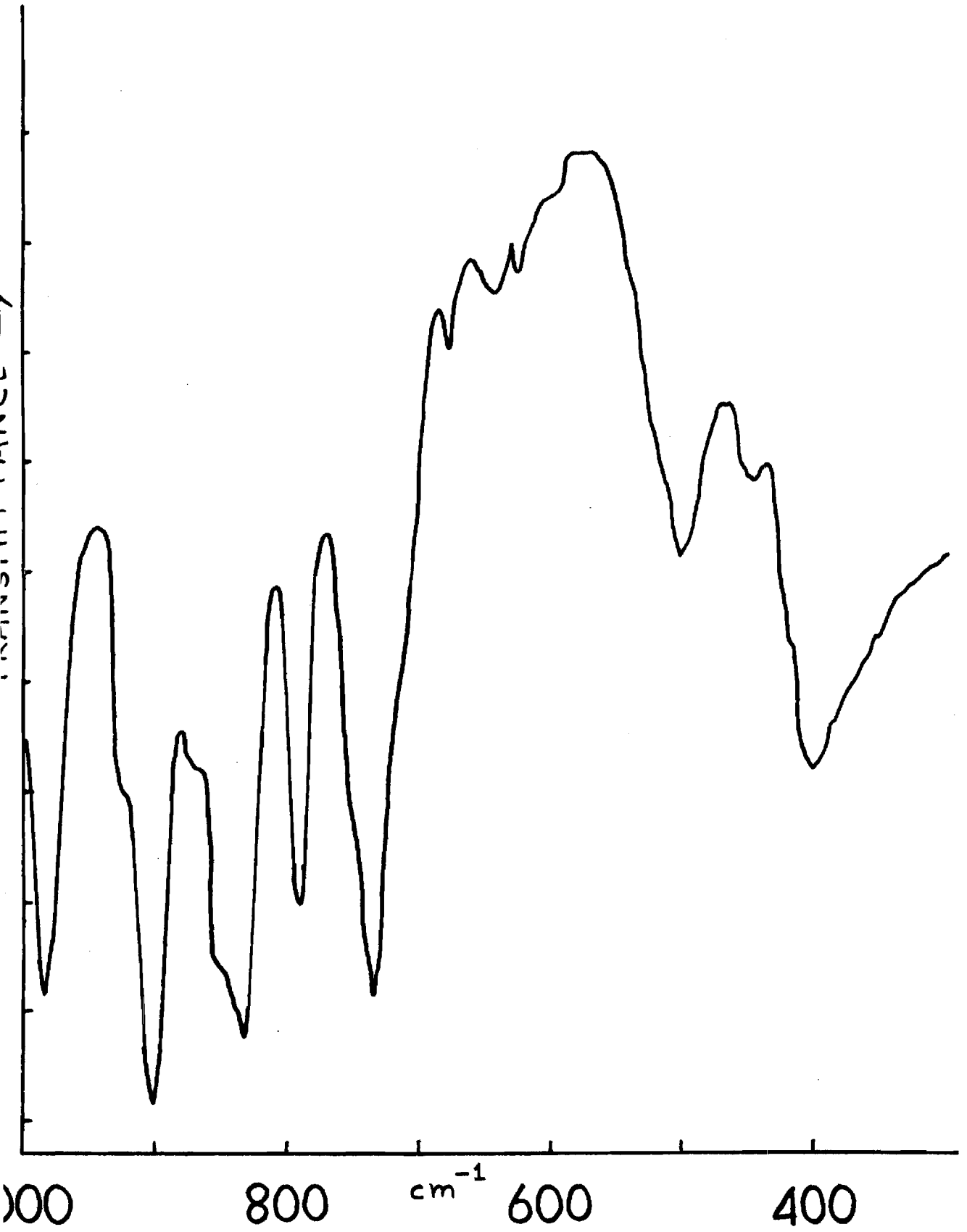
Figure 1. Infrared spectra of CH_3Li, $(CH_3)_2Be$ and mixtures of CH_3Li and $(CH_3)_2Be$ in Diethyl Ether. (a) CH_3Li; (b) $(CH_3)_2Be$; (c) 1:1 CH_3Li + $(CH_3)_2Be$; (d) 2:1 CH_3Li + $(CH_3)_2Be$; (e) 3:1 CH_3Li + $(CH_3)_2Be$; (f) 1:2 CH_3Li + $(CH_3)_2Be$


(a)
TRANSMITTANCE →
000
800
cm⁻¹
600
400

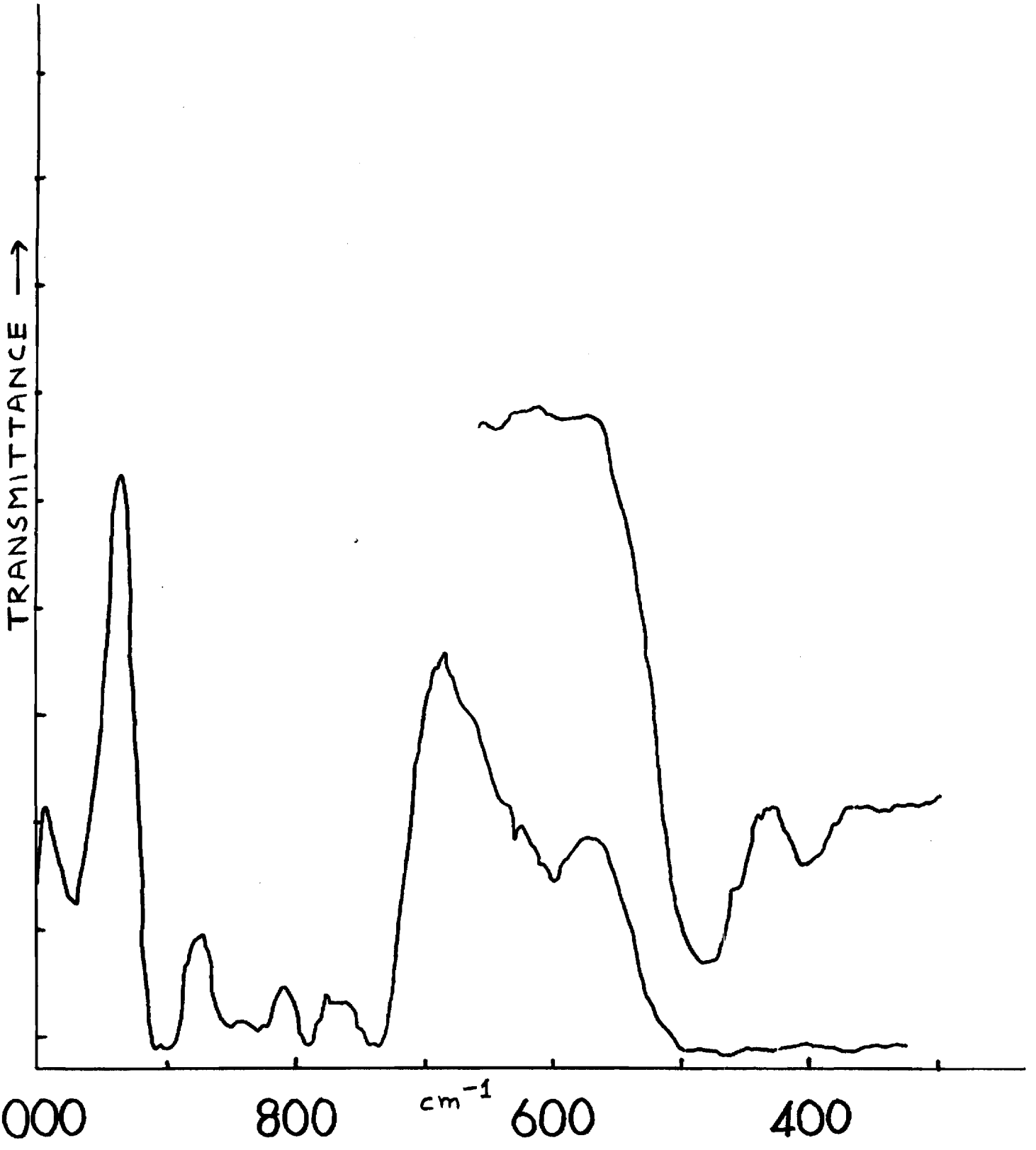
(b)

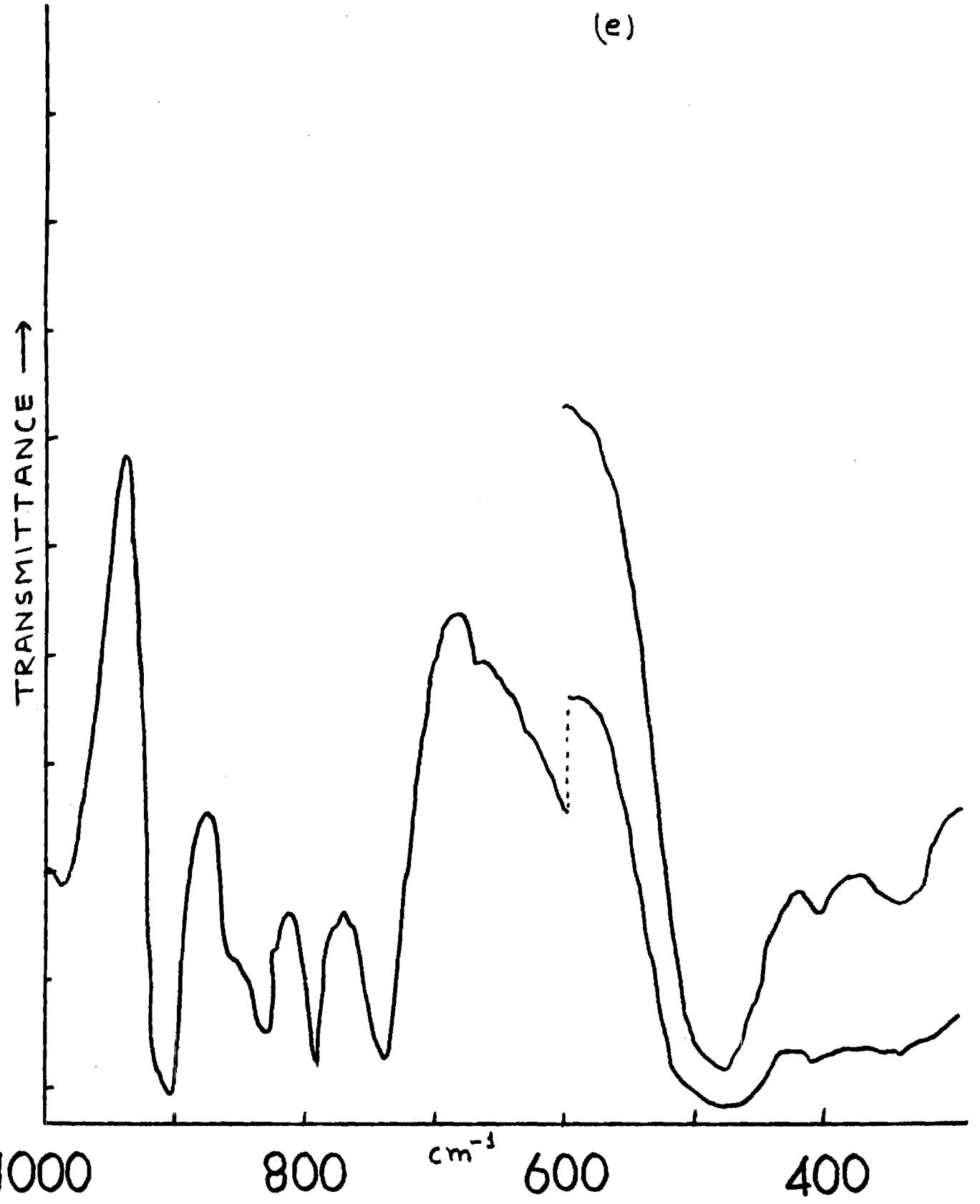


(c)



(d)




(e)
TRANSMITTANCE →
1000
800
cm⁻¹
600
400

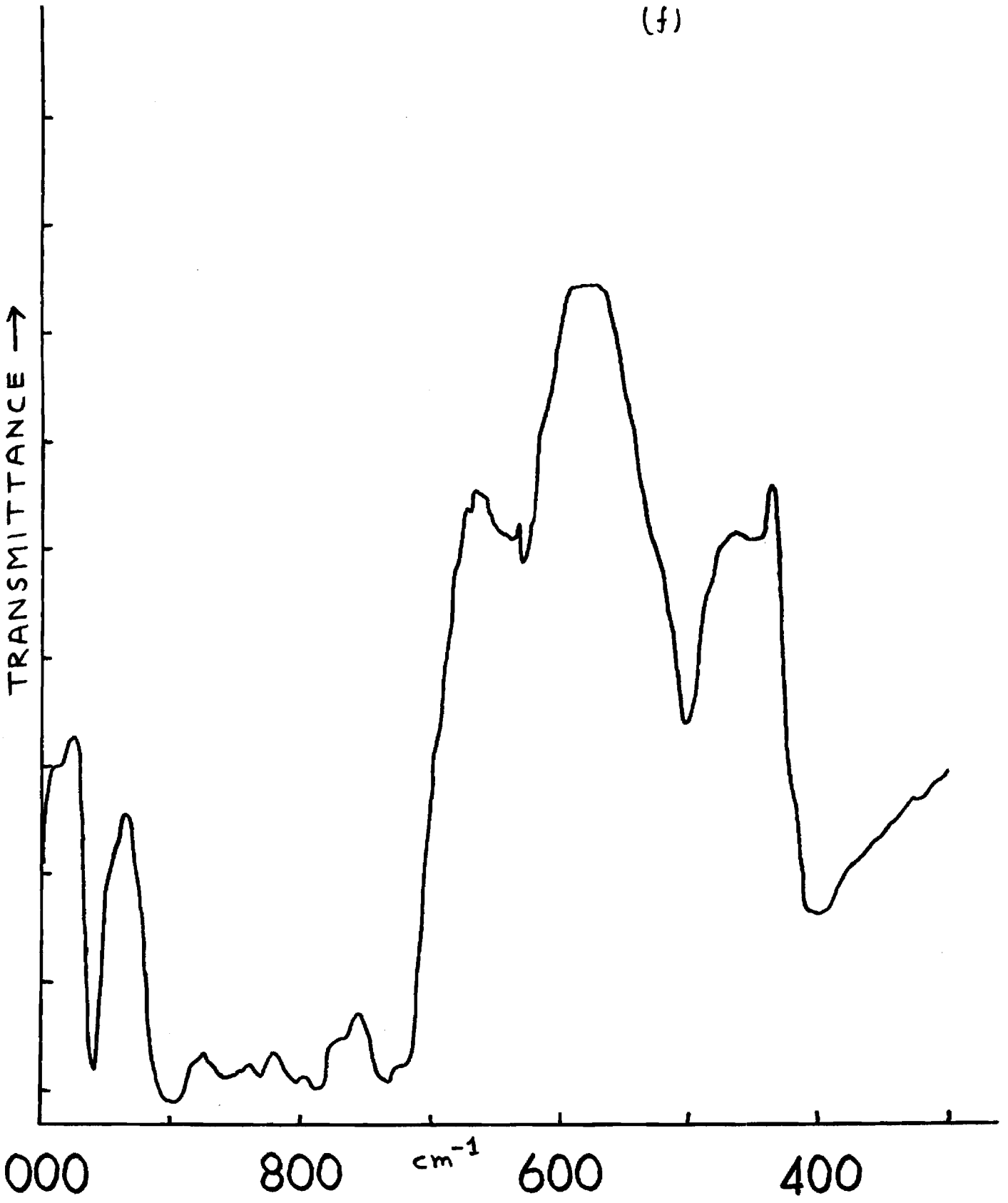

(f)
TRANSMITTANCE →
000
800
cm⁻¹
600
400

Figure 2. Proton nmr spectra of (a) $(CH_3)_2Be$; (b) CH_3Li; (c) 1:1 $CH_3Li + (CH_3)_2Be$; (d) 2:1 $CH_3Li + (CH_3)_2Be$ (e) 3:1 $CH_3Li + (CH_3)_2Be$ in Diethyl Ether at room temperature.

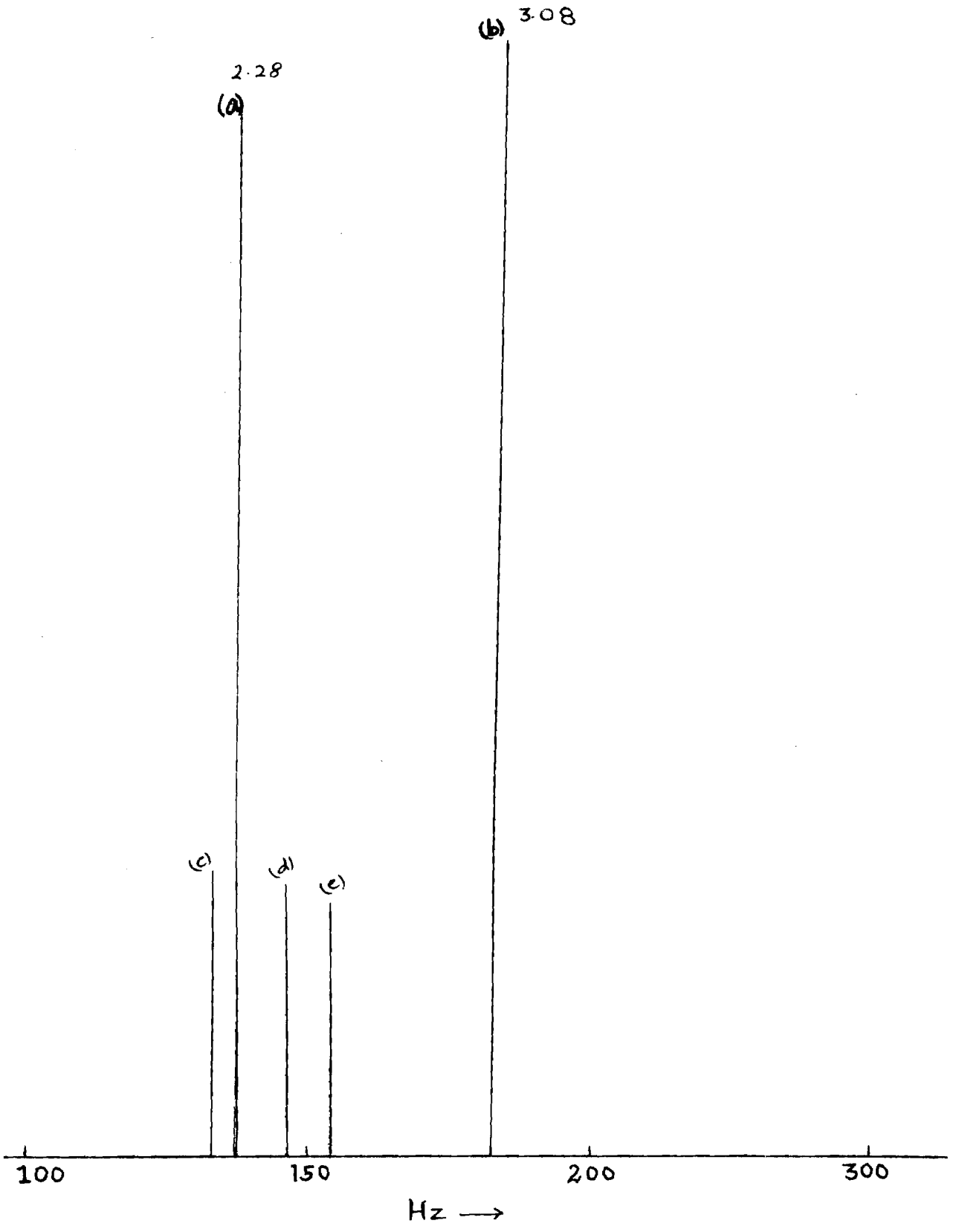

(b) 3.08
2.28
(a)
(c)
(d)
(e)
100
150
200
300
Hz ⟶

Figure 3. Proton nmr spectra of $CH_3Li + (CH_3)_2Be$ in Diethyl Ether (a) at -65°; (b) at -96°

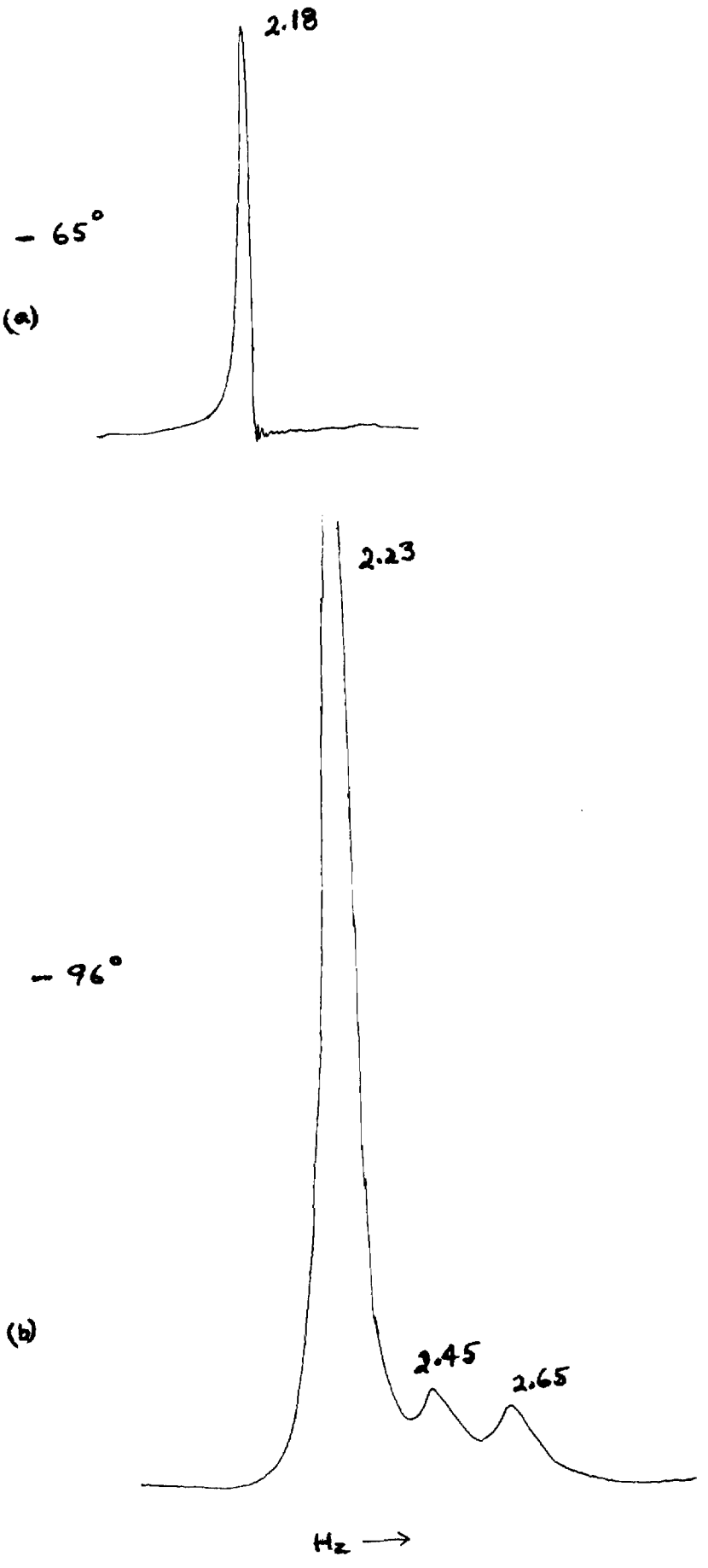

2.18
- 65°
(a)
2.23
- 96°
(b)
2.45
2.65
Hz →

Figure 4. Proton nmr spectra of $2CH_3Li + (CH_3)_2Be$ in Diethyl Ether (a) at -65°; (b) at -96°

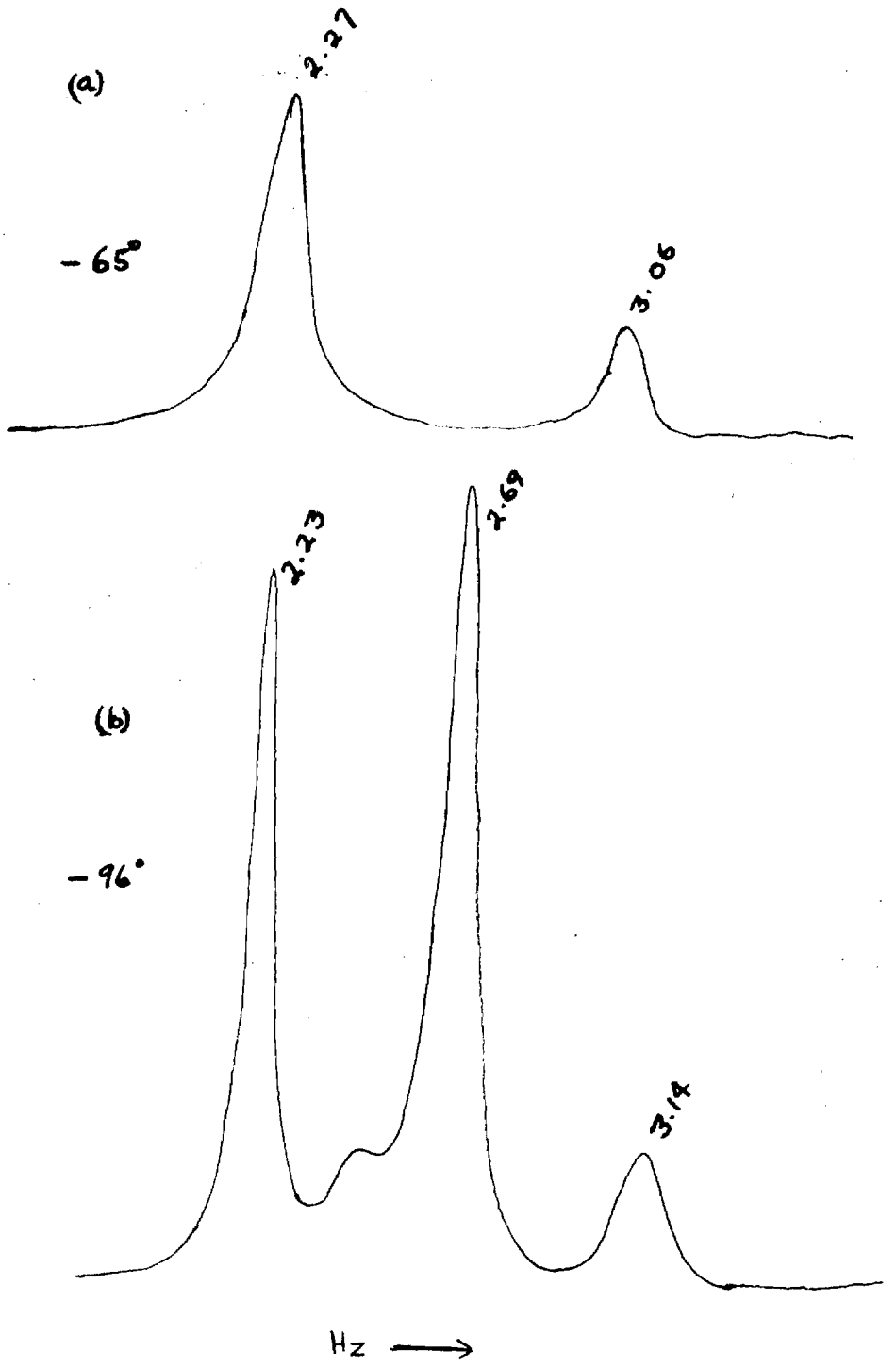

(a)
-65°
2.27
3.06
(b)
-96°
2.23
2.69
3.14
Hz

Figure 5. Proton nmr spectra of $3CH_3Li + (CH_3)_2Be$ in Diethyl Ether (a) at -65°; (b) at -96°

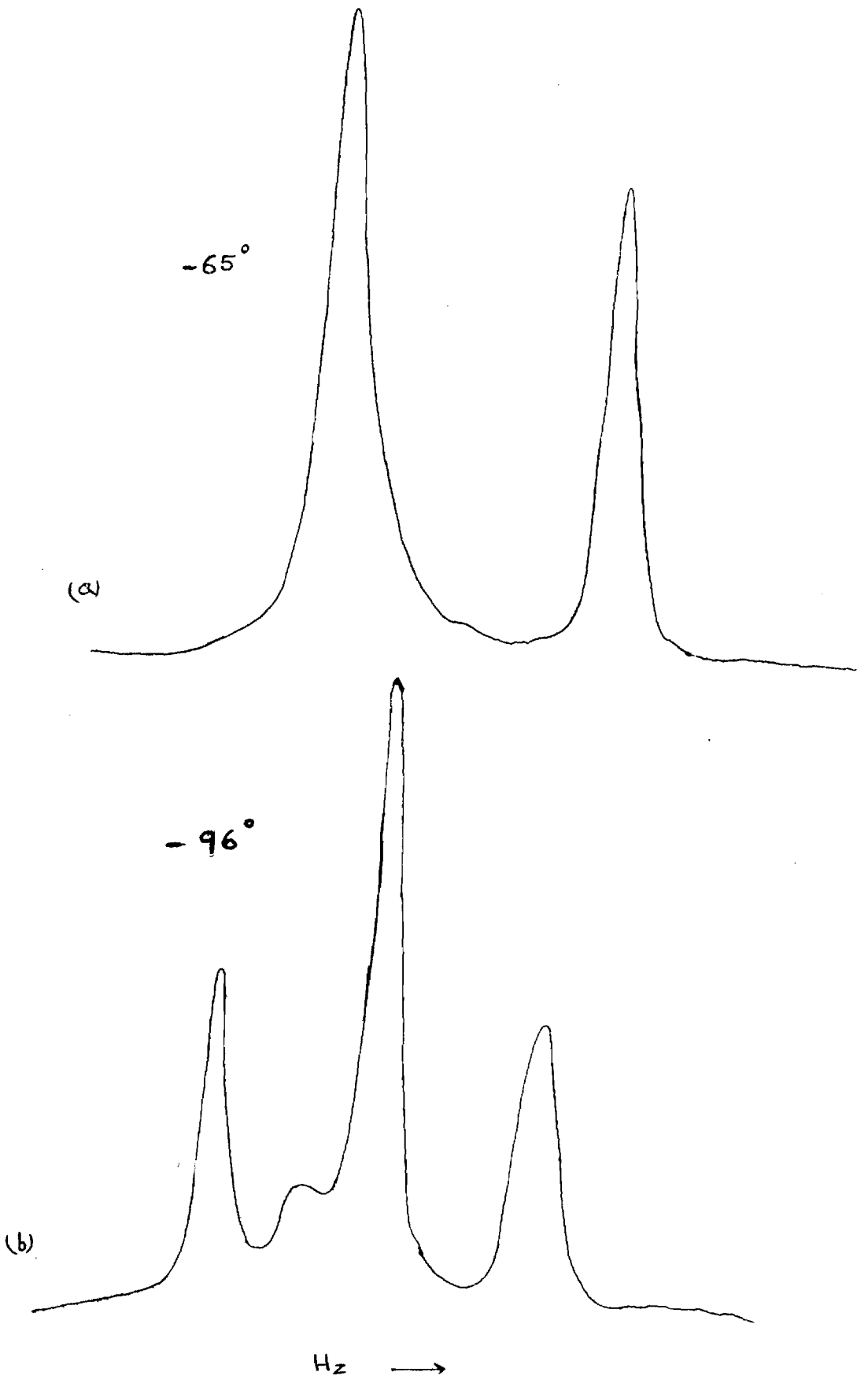

-65°
(a)
-96°
(b)
Hz ⟶

Figure 6. Vacuum DTA-TGA of BeH_2

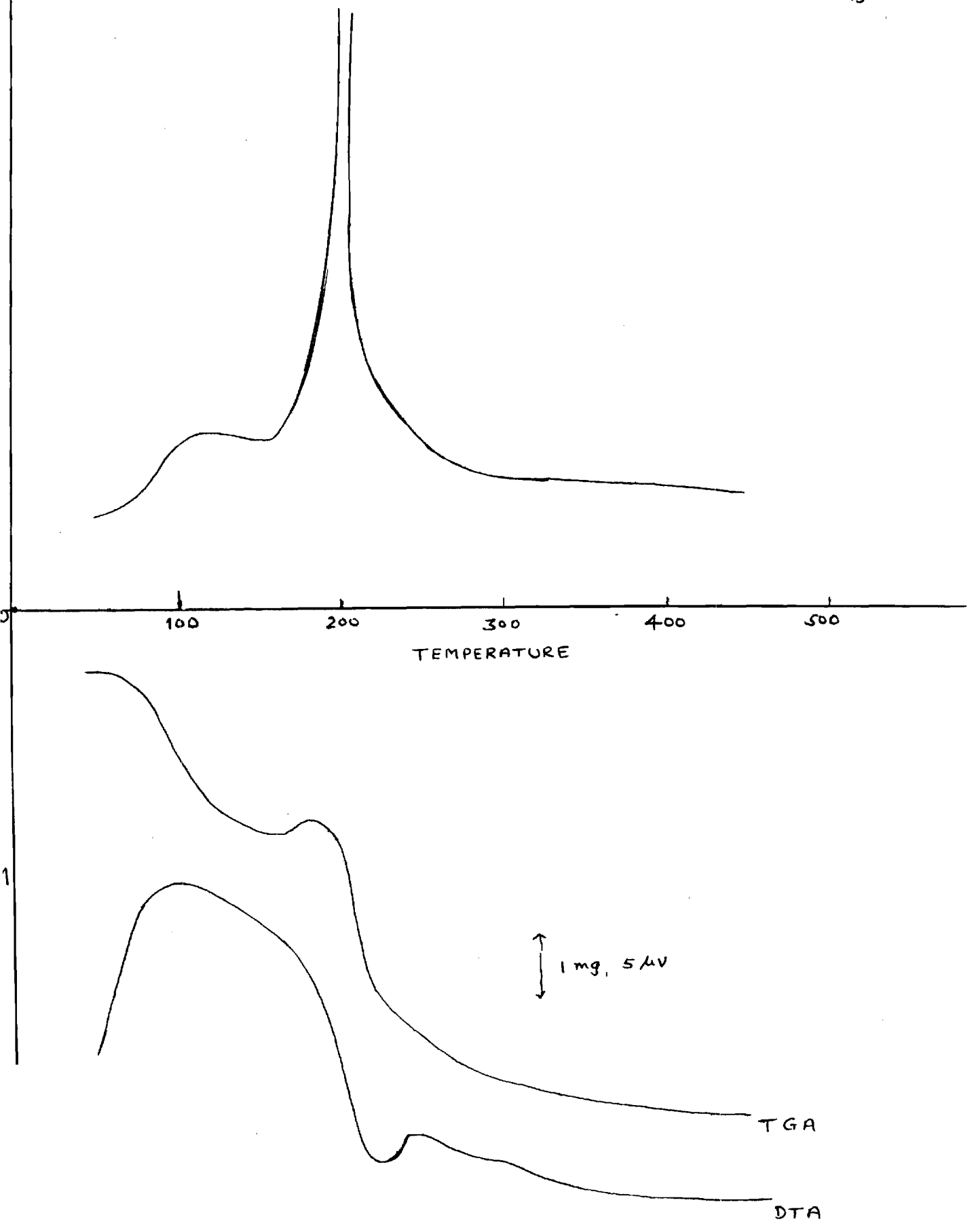

100
200
300
400
500
TEMPERATURE
1 mg, 5 μV
TGA
DTA

Figure 7. Vacuum DTA-TGA of Li_2BeH_4

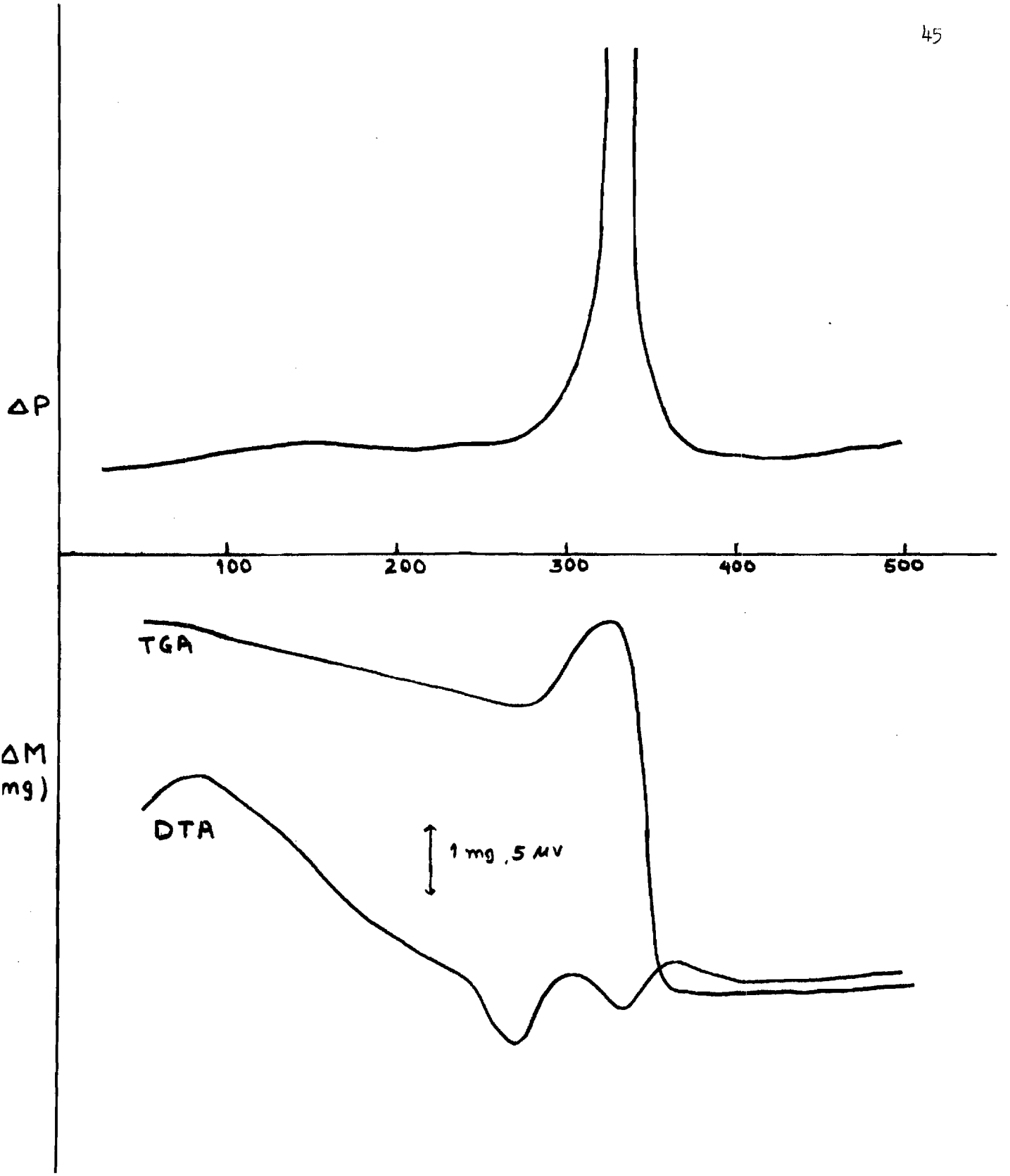
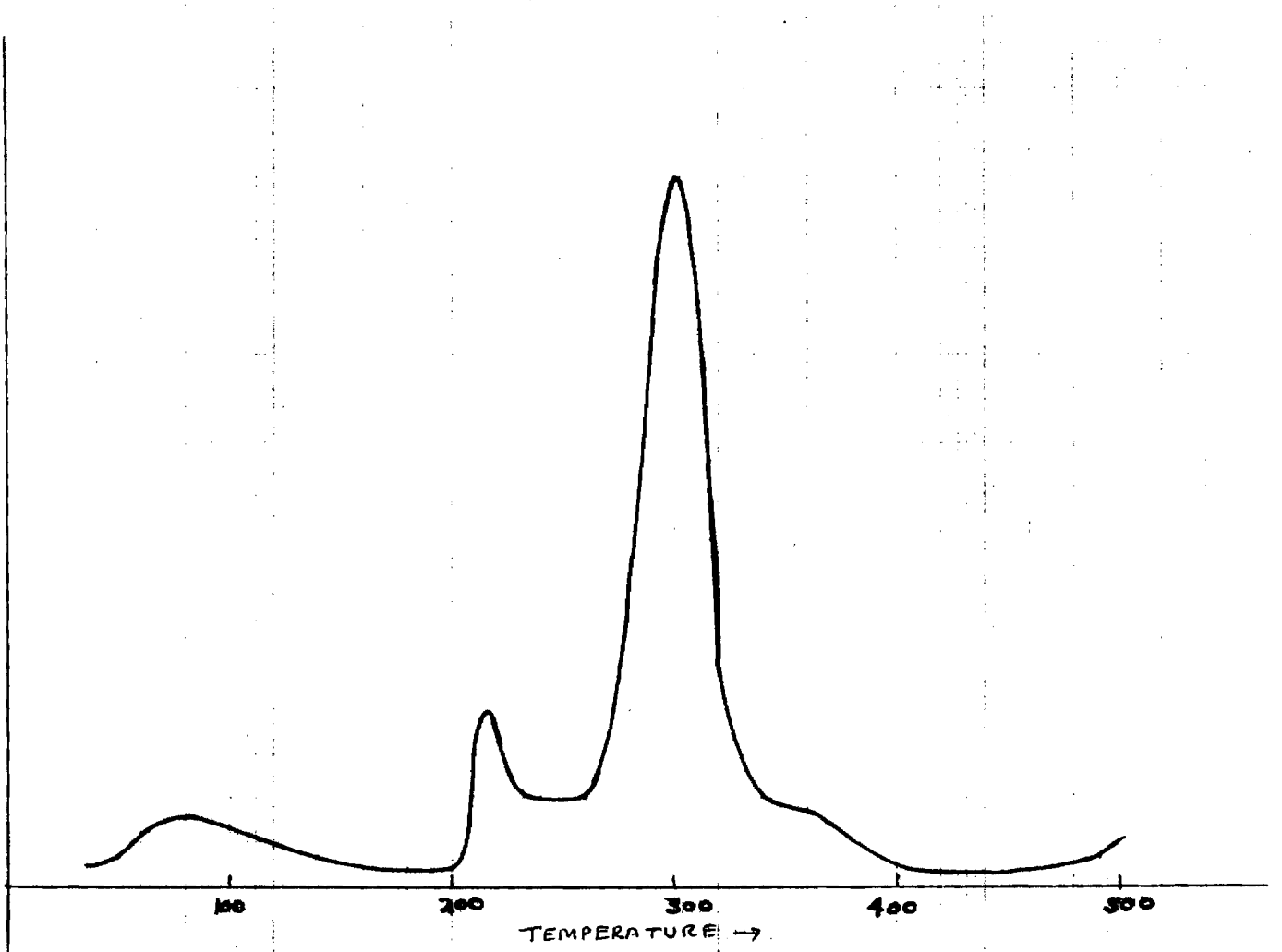

ΔP
100
200
300
400
500
TGA
ΔM
mg)
DTA
1 mg , 5 MV

Figure 8. Vacuum DTA-TGA of Li_3BeH_5


100
200
300
400
500
TEMPERATURE →

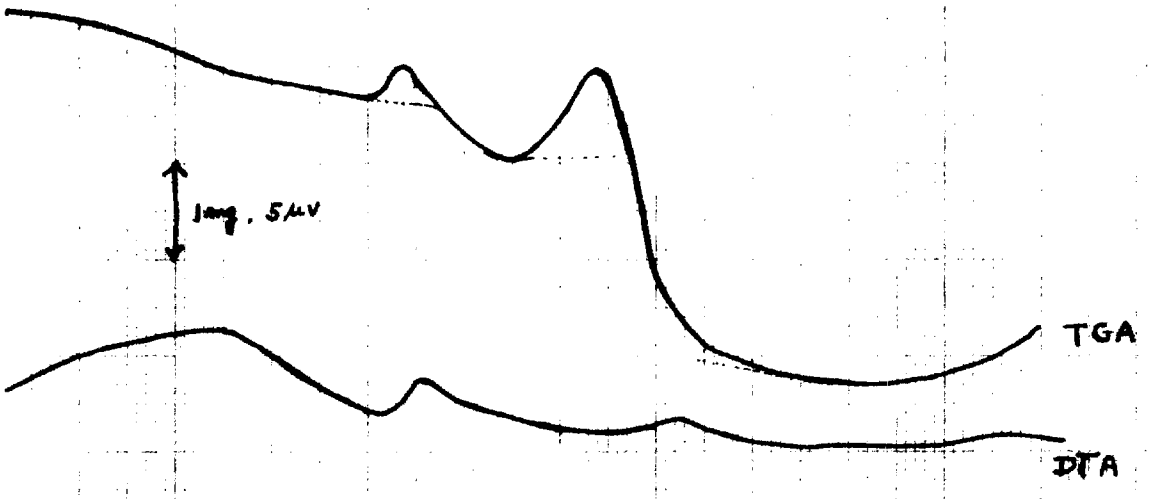

1 mg . 5 μV
TGA
DTA

Table 1. X-Ray Powder Pattern d-Spacing Data

LiH		BeH_2		Li_2BeH_4		Li_3BeH_5	
d,A	I/Io	d,A	I/Io	d,A	I/Io	d,A	I/Io
3.85	w	3.85	s	3.85	w	3.65	w
2.65	w	3.45	w	3.69	vw	3.48	s
2.60	w	2.32	s	3.52	w	2.92	s
2.35	s	2.275	uvw	3.25	w	2.75	ms
2.25	m	2.225	vvw	2.95	s	2.55	w
2.03	s	2.17	w	2.80	vw	2.42	w
1.95	w	2.02	w	2.57	s	2.30	vw
1.59	w	1.96	ms	2.40	w	2.18	vvw
1.440	s	1.72	w	2.32	vw	2.02	vvw
1.225	m			2.17	vw	1.80	vvw
1.175	w			2.04	w		
0.935	w			1.96	m		
0.911	w			1.81	s		
				1.55	ms		
				1.47	w		

Table II. Chemical Shifts w.r.t. Center of Methyl Triplet of Diethyl Ether

Sample	Chemical Shifts (in p.p.m.)			
	RT	-65°	-96°	
CH_3Li	3.08	3.08		
$(CH_3)_2Be$	2.28	2.38	2.550	
$CH_3Li + (CH_3)_2Be$	2.21	2.22	2.25 (128) 2.67 (6)	
$2CH_3Li + (CH_3)_2Be$	2.40	2.27 (46) 3.07 (14)	2.23 (82) 2.69 (134) 3.14 (22)	
$3CH_3Li + (CH_3)_2Be$	2.55	2.30 (26) 3.08 (13)	2.23 (50) 2.70 (150) 3.15 (63)	
$4CH_3Li + (CH_3)_2Be$	2.62	2.31 (31) 3.07 (28)	2.22 (48) 2.68 (138) 3.13 (122)	
$CH_3Li + 2(CH_3)_2Be$			2.34	
$CH_3Li + 3(CH_3)_2Be$			2.35	
$6CH_3Li + (CH_3)_2Be$			2.19 (20) 2.64 (32) 3.11 (90)	

Concerning the Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc. III. Proton NMR Study of the Reaction Product of $(CH_3)_2Zn$ with $LiAlH_4$ and AlH_3 in Tetrahydrofuran.

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ABSTRACT

Proton nmr spectra of THF solutions of $(CH_3)_2Zn$, $Li(CH_3)_2ZnH$, $Li(CH_3)_2ZnAlH_4$, $Li(CH_3)_4Zn_2H$ and $Li(CH_3)_4Zn_2AlH$ have been examined at room temperature as well as at low temperatures. Dimethylzinc and $Li(CH_3)_2ZnH$ are found to be monomeric in THF whereas a rapid chemical exchange process between two or more species occurs for $Li(CH_3)_4Zn_2H$ in THF. The complexes $Li(CH_3)_2ZnAlH_4$ and $Li(CH_3)_4Zn_2AlH_4$ exist as an equilibrium mixture of at least three different species in THF. It is concluded that the reactions of $LiAlH_4$ and $(CH_3)_2Zn$ in 1:1 and 1:2 molar ratios are faster than the reactions of $Li(CH_3)_2ZnH$ and $Li(CH_3)_4Zn_2H$ with AlH_3.

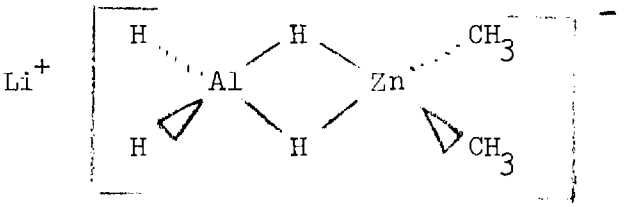
INTRODUCTION

The synthesis of triple metal hydrides involving an alkali metal, zinc and aluminum, namely, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ have been reported very recently.[1,2] These complexes were formed either by the

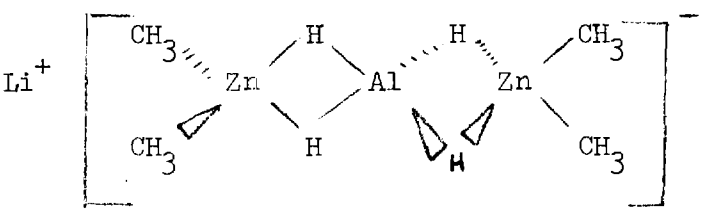
(1) John J. Watkins and E.C. Ashby, submitted for publication.

(2) John J. Watkins and E.C. Ashby, submitted for publication.

reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ or by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in 1:1 or 1:2 molar ratio. The following structures have been assigned to these complexes on the basis of infrared studies of these compounds in THF.



I



II

Several mechanisms[1,2] have been proposed for the formation of I and II by thr reaction of $(CH_3)_2Zn$ with either AlH_3 or $LiAlH_4$ in appropriate mole ratios in THF.

The present work describes a detailed proton nmr study of the following reactions to understand the mechanism of the formation of

$$(CH_3)_2Zn + LiH \longrightarrow Li(CH_3)_2ZnH \quad (1)$$

$$Li(CH_3)_2ZnH + AlH_3 \longrightarrow Li(CH_3)_2ZnAlH_4 \quad (2)$$

$$2(CH_3)_2Zn + LiH \longrightarrow Li(CH_3)_4Zn_2H \quad (3)$$

$$Li(CH_3)_4Zn_2H + AlH_3 \longrightarrow LiZn_2(CH_3)_4AlH_4 \quad (4)$$

$$(CH_3)_2Zn + LiAlH_4 \longrightarrow LiZn(CH_3)_2AlH_4 \quad (5)$$

$$2(CH_3)_2Zn + LiAlH_4 \longrightarrow LiZn_2(CH_3)_4AlH_4 \quad (6)$$

complexes I and II and also to characterize the intermediates involved in the above reactions.

EXPERIMENTAL SECTION

All operations were carried out in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture.[3]

(3) E.C. Ashby and R.D. Schwartz, J. Chem. Ed., 51, 65 (1974).

Instrumentation and Analytical Procedures. Proton spectra were obtained at 60 M Hz using A60 spectrometer and 100 M Hz using JEOL 4H-100 spectrometer. The low temperatures were obtained using the standard low-temperature accessories supplied by Varian Associates. The system was allowed to come to equilibrium at each temperature before the spectrum was recorded. A standard 5 mm (outer diameter) thin wall, high resolution nmr tube was used for all the measurements.

Gas analyses was carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum and Zinc analyses were carried out by complexiметric titration with EDTA. Lithium analysis was carried out by flame photometry. Analysis for carbon bonded and oxygen-bonded metals were carried out by Watson and Eastham[4] method using

(4) S.C. Watson and J.F. Eastham, J. Organometal. Chem., 9, 165 (1967).

2,2'-biquinoline and phenolphthalein indicators.

Materials. Tetrahydrofuran (Fisher certified reagent) was pre-dried over sodium wire and then distilled over $NaAlH_4$ prior to use. Lithium aluminum hydride was obtained as gray powder from Ventron, Metal hydrides Division. Solution of $LiAlH_4$ in THF was prepared by stirring the solid hydride for 24 hours with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. Aluminum hydride was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration resulting in a clear and colorless solution of AlH_3 in THF.[5]

(5) H.C. Brown and H.M. Yoon, J. Amer. Chem. Soc., 88, 1464 (1966).

Lithium hydride was obtained by hydrogenolysis of t-butyllithium at room temperature at 4000 psi for 24 hours. The white solid was washed with dry benzene and a slurry of LiH in THF was made. Dimethylzinc was prepared by the modified method of Noller[6] already reported in the literature.[1,2]

(6) C.R. Noller, Org. Syn., 12, 86 (1932).

Preparation of NMR Samples. After the concentrations (usually about 1 M lithium hydride, 0.5 M dimethylzinc, 0.5 M $LiAlH_4$ and 0.3 M for AlH_3) of the separate solutions were determined, they were mixed in the appropriate volume proportions to form the required compound. The reactions are described in detail elsewhere.[1,2] The solutions were transferred into standard nmr tubes and stored in Dry Ice.

Reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in THF at -78° and Preparation of NMR

Sample. To 10 ml (3.44 mmole) of dimethylzinc solution in THF cooled at -78°, 8.1 ml (3.44 mmole) $LiAlH_4$ solution in THF was added slowly under nitrogen atmosphere. The mixture was stirred for 5 hours at -78°. The resultant clear solution was then transferred into a NMR tube which was flushed with nitrogen and then immediately stored in Dry Ice.

Results and Discussion

Reaction of $(CH_3)_2Zn$ with LiH. (a) In 1:1 Mole Ratio. When a slurry of LiH in THF is added to a solution of $(CH_3)_2Zn$ in THF, a clear solution is obtained after stirring the mixture for a few minutes. The infrared spectrum of the resultant solution shows a broad band centered on 1450 cm^{-1} (Figure 1). This band may be assigned to terminal Zn-H st. vibration on the basis of the results already reported in the literature.[7,8] The proton nmr spectrum

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(7) George J. Kubas and D.F. Shriver, J. Amer. Chem. Soc., 92, 1949 (1970).

(8) N.A. Bell and G.E. Coates, J. Chem. Soc., A, 823 (1968).

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of the solution shows a sharp single resonance peak at 2.85 ppm upfield from the center of β-hydrogen multiplets in THF at all temperatures. This resonance peak is assigned to the methyl protons of the complex $LiZn(CH_3)_2H$. An attempt to locate the signal due to hydridic proton failed due to interference by the solvents peaks. Kubas and Shriver[7] have studied the proton nmr spectra of several dialkyl and diarylzinc hydride complexes in various solvents. It has been found that in dimethoxyethane, $LiZn(CH_3)_2H$ shows hydridic proton signal at 5.44 ppm downfield from tetramethylsilane. In order to gain further insight into the molecularity of these complexes,

these authors also determined the molecular weight of $NaZn(CH_3)_2H$ in THF. For ionic complexes of this type, the determination of molecular weight may be complicated by partial dissociation of ion pairs and coordination of solvent to zinc or alkali metal ions. The former may not be a serious problem because of the evidence[9] of such compounds to exist mainly as

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(9) C. Carvajal, K.L. Tolle, J. Smid and M. Szwarz, J. Amer. Chem. Soc., 87, 5548 (1965).

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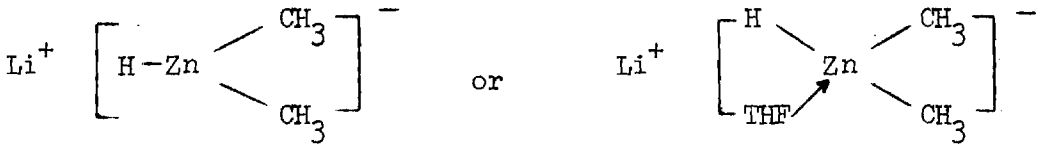
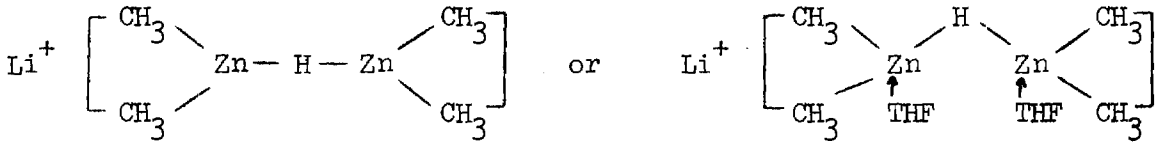
solvent-separated ion pairs in THF. However, coordination of solvent to solute leads to a larger vapour pressure depression than expected in the absence of coordination. Assuming up to five moles of solvent to coordinate to a compound of the type $NaHZnR_2$, a monomeric structure has been suggested for these complexes. Thus, $LiZn(CH_3)_2H$ being similar to $NaZn(CH_3)_2H$, can be written as:



(b) In 2:1 Mole Ratio. Dimethylzinc reacts with lithium hydride in 2:1 mole ratio in THF to yield a clear solution. The infrared spectrum of the resultant solution shows a broad band centered on 1300 cm^{-1} (Figure 1) which may be assigned to Zn-H st. vibration. The fact that this band has shifted to lower frequency by about 100 cm^{-1} indicates the presence of bridging hydrogen. The proton nmr spectrum of the resultant solution

again shows a sharp single resonance peak at about 2.8 ppm upfield from β-hydrogen multiplets of THF at all temperatures. The signal due to hydridic proton is masked by the strong solvent peaks. It has already been reported in the literature[7] that in the 1:2 complex, a hydridic rather than a methyl bridge is involved in the formation of the complex. The complex $LiZn_2(CH_3)_4H$ may therefore, have the structure



It is also possible for the complex $LiZn_2(CH_3)_4H$ to have an equilibrium involving a 1:1 adduct and a hydride-bridged, 1:2 adduct.

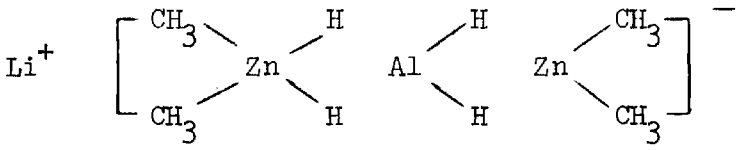
$$Li^+HZn(CH_3)_2^- + Zn(CH_3)_2 \rightleftharpoons Li^+(CH_3)_2ZnHZn(CH_3)_2^- \qquad (7)$$

In order to slow chemical exchange and observe resonances due to individual species in solution, low temperature proton nmr spectrum was obtained. It has been found that even down to the freezing point of THF, a single sharp resonance peak occurs indicating a rapid exchange. However, Kubas and Shriver[7] have been able to obtain the proton nmr spectrum of $LiZn(CH_3)_4H$ in 2-methyltetrahydrofuran (mp < -90°), which shows two types of hydridic protons arising from 1:1 and 1:2 species.

Reaction of AlH_4 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$. When AlH_3 was allowed to react with $LiZn(CH_3)_2H$ in THF, no precipitation occurred. The infrared spectrum of the resultant mixture shows a strong band at 1660 cm^{-1}

which may be assigned to terminal Al-H st. vibration and the broad band at 1400 cm^{-1} may be assigned to Zn-H st. vibration. The proton nmr spectrum of the resultant solution shows a sharp resonance line at room temperature which indicates either the presence of a single compound in solution or a rapid exchange between different species in solution. The low temperature nmr spectrum of the solution shows a triplet (Table 1) at -63°. It is interesting to note that the intensities of resonance peaks change with time. No appreciable change in the position of the respective peaks was observed when the mixture was allowed to stand for a week at Dry Ice temperature. When the mixture was allowed to stand at room temperature, there was gradual precipitation of zinc hydride which immediately decomposed to metallic zinc and hydrogen and the mixture became black. The proton nmr spectrum of the clear solution obtained after filtration of black precipitate, gave a broad signal at room temperature and multiplets at low temperature. Therefore, it seems that in solution there is more than one kind of specie present and an alkyl-hydrogen exchange reaction is taking place. Unfortunately an attempt to characterize the different species in solution proved unfruitful due to closeness of methyl proton signals in trimethylaluminum and its derivatives and dimethylzinc.

The reaction of AlH_3 with $LiZn_2(CH_3)_4H$, like the reaction of $LiZn(CH_3)_2H$ with AlH_3, yields a clear solution. The infrared spectrum of the reaction mixture showed only a broad band centered on 1400 cm^{-1}. This band may be assigned to bridging metal-hydrogen st. vibration as is shown in the structure of the complex $LiZn(CH_3)_4H$ proposed previously.[1]



The proton nmr spectrum of the above reaction mixture shows a triplet at room temperature and a doublet at low temperatures. This again implies an equilibrium between one or more species in solution. The intensities of the peaks remained unchanged even after six days of storing the sample in Dry Ice.

Reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in THF. (a) In 1:1 Mole Ratio. When a solution of $LiAlH_4$ in THF was added to a solution of $(CH_3)_2Zn$ in 1:1 mole ratio, a clear solution was obtained. The infrared spectrum of the resultant solution was identical with the infrared spectrum of $LiZn(CH_3)_2AlH_4^+$ obtained by the reaction of AlH_3 with $LiZn(CH_3)_2H$ in THF. The proton nmr spectrum of the solution showed a triplet (Table) at room temperature as well as at low temperatures indicating the presence of more than one specie in the solution. It is interesting to note at this point that the proton nmr spectrum of complex $LiZn(CH_3)_2AlH_4$[10] shows a sharp single

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(10) $LiZn(CH_3)_2AlH_4$ prepared by the reaction of AlH_3 with $LiZn(CH_3)_2H$ in THF.

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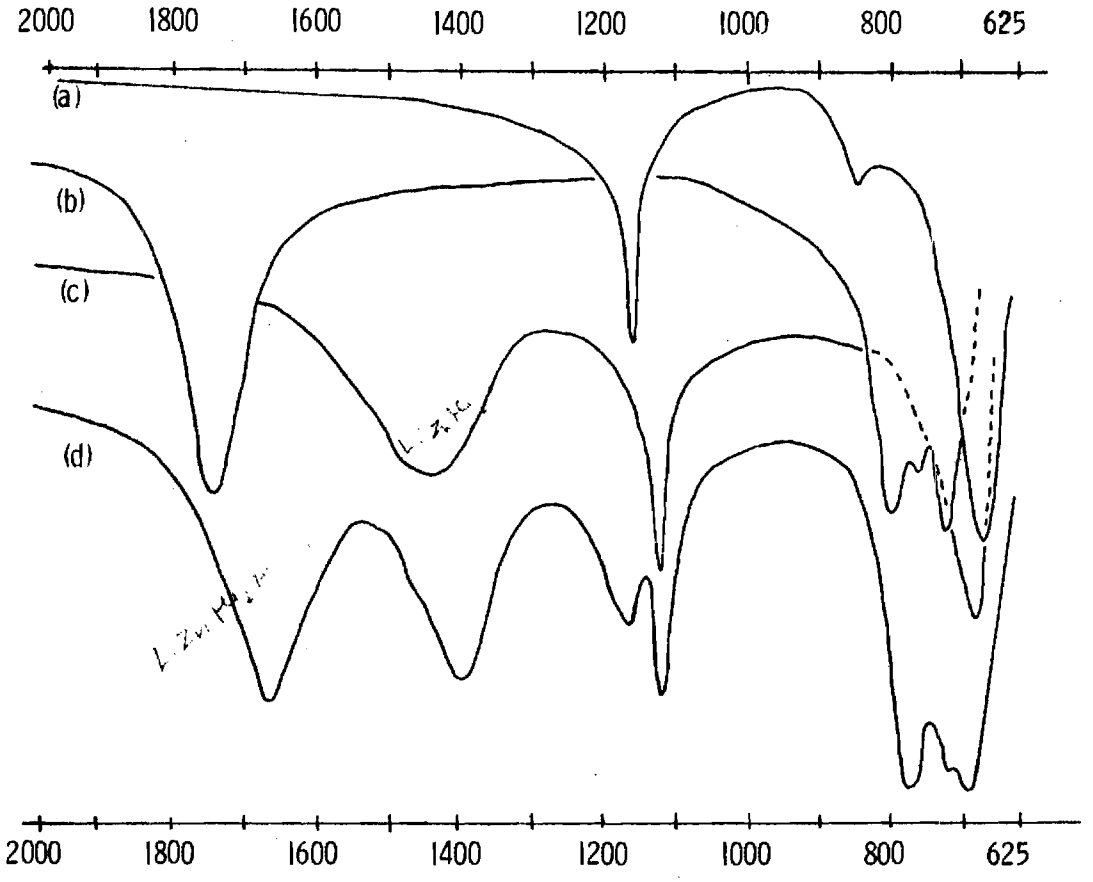
resonance peak at room temperature. Therefore, it appears that the formation of complex $LiZn(CH_3)_2AlH_4$ by the reaction of $LiAlH_4$ and $(CH_3)_2Zn$ is faster than the reaction of AlH_3 and $LiZn(CH_3)_2H$. To

varify the above statement, the above reaction was performed at -78° and the proton nmr spectrum was recorded immediately. The protonnnmr spectrum again showed a triplet which indicates the presence of one or more specie in equilibrium.

(b) In 1:2 Mole Ratio. $LiAlH_4$ reacts with $(CH_3)_2Zn$ in 1:2 mole ratio to yield a clear solution. The infrared spectrum of the clear solution shows a broad band at ~ 1400 cm^{-1} which may be assigned to metal-hydrogen St. vibration. The proton nmr spectrum of the clear solution shows a triplet at room temperature as well as low temperature. There is no appreciable change in the position of the resonance peaks and the relative intensities remain the same. It is therefore concluded that the complexes $LiZn(CH_3)_2AlH_4$ and $LiZn(CH_3)_4AlH_4$ obtained by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn(CH_3)_4H$ are the same as obtained by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$. Furthermore, in solution there are more than one specie present at equilibrium.

Figure 1. Infrared Spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn(CH_3)_2H$ in THF, (d) $LiZn(CH_3)_2AlH_4$ in THF.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(a)
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800
625

Figure 2. Infrared Spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn_2(CH_3)_4H$ in THF, (d) $LiZn_2(CH_3)_4AlH_4$ in THF.

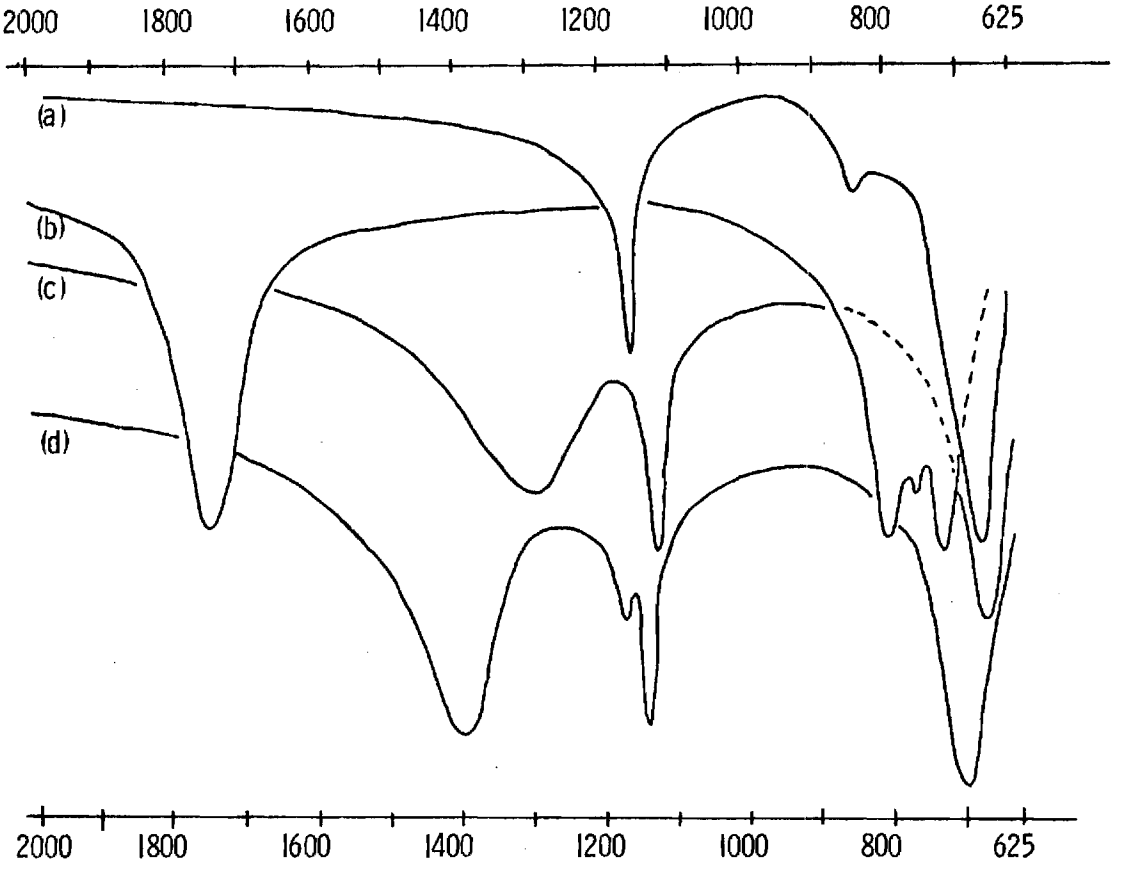
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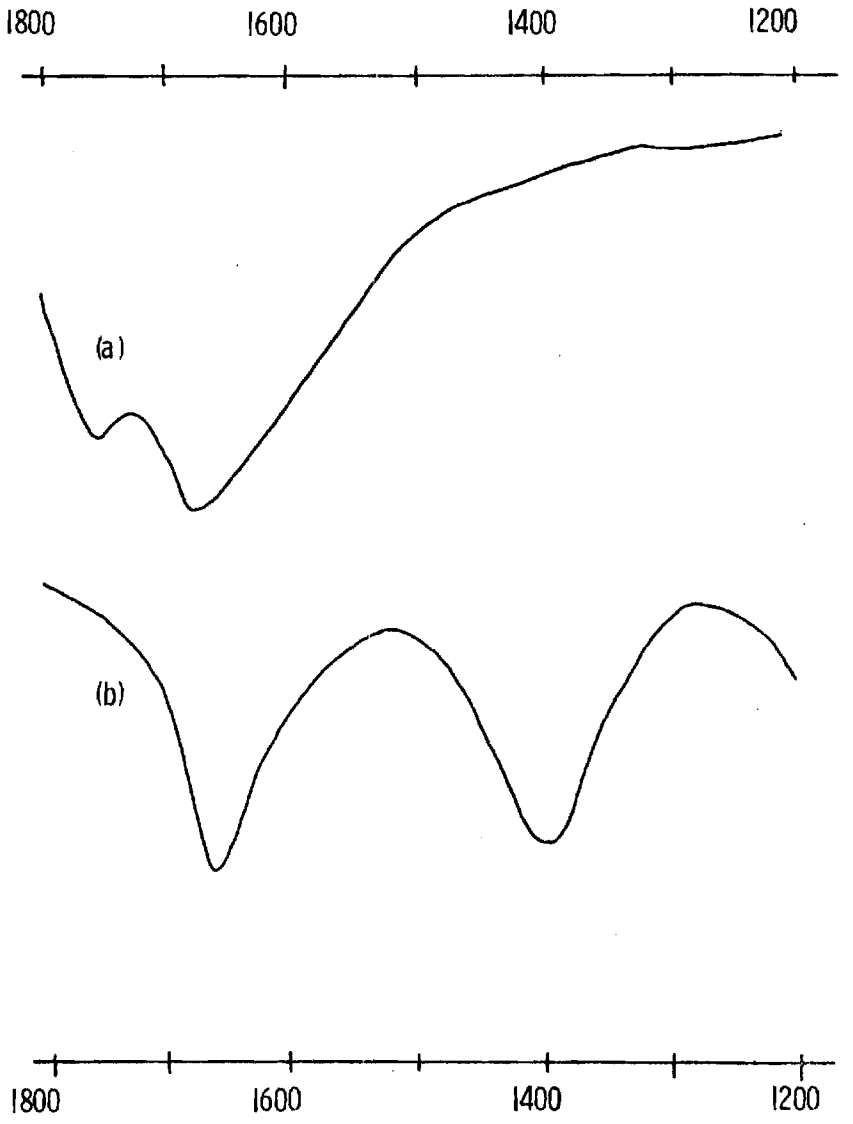
Figure 3. 1800-1200 cm^{-1} Region of the Infrared Spectrum for (a) AlH_3 in THF, (b) $LiZn(CH_3)_2H$ in THF, (c) $LiZn(CH_3)_2AlH_4$ in THF, (d) $LiZn_2(CH_3)_4H$ in THF, (e) $LiZn_2(CH_3)_4AlH_4$ in THF.


1800
1600
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(a)
(b)
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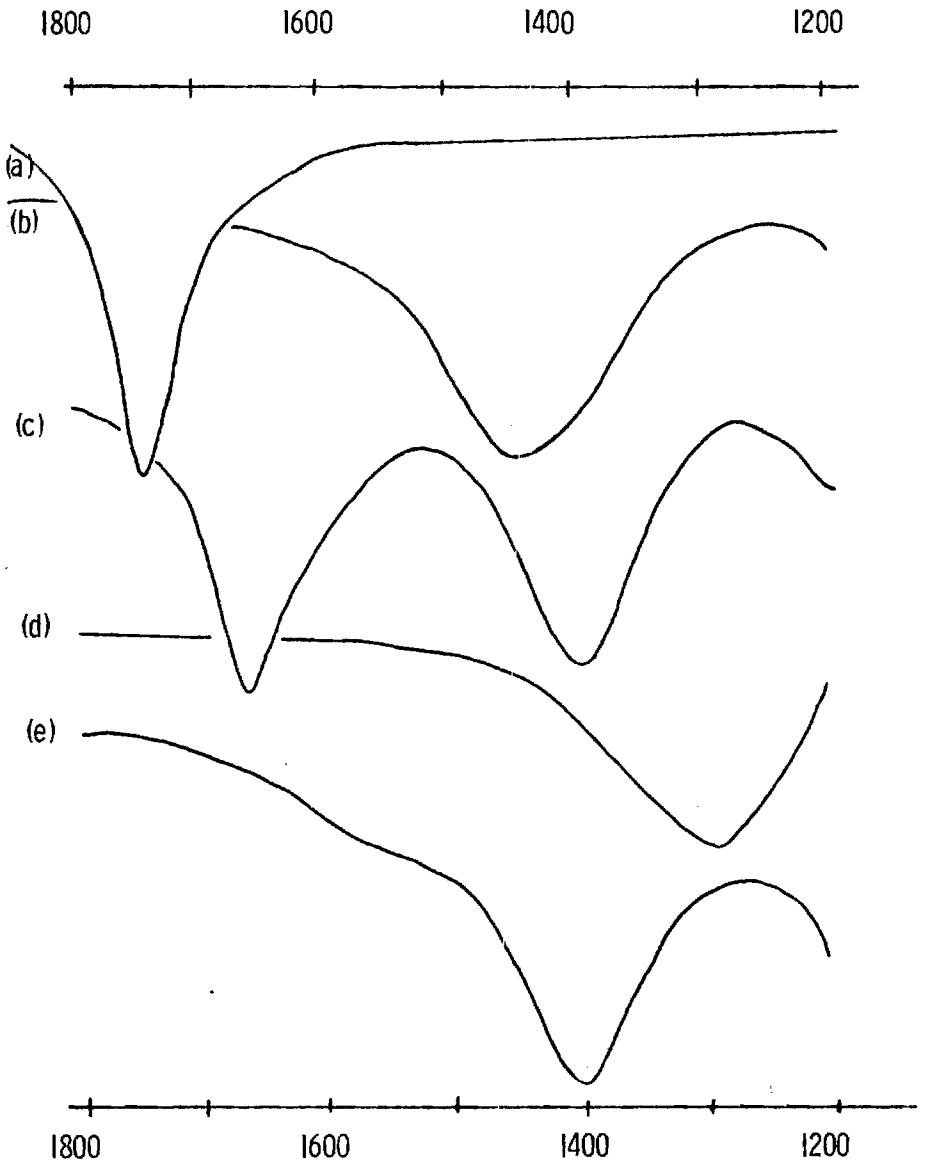
1400
1200

Figure 4. 1800-1200 cm^{-1} Region of the Infrared Spectrum for (a) 2:1:1 Mixture of $(CH_3)_2AlH$, $LiAlH_4$, and $LiAl(CH_3)_2H_2$ in THF, (b) $LiZn(CH_3)_2AlH_4$ in THF.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(a)
(b)
(c)
(d)
(e)
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1600
1400
1200

Table 1. H NMR Study of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc

CHEMICAL SHIFTS

	Compounds	Room Temp.			Low Temp. (-63°C)					
		3 hrs.			3 hrs.	24 hrs.	48 hrs.	4 days	5 days	6 days
1.	Me_2Zn	2.633			2.785	2.800				
2.	$LiH + Me_2Zn$ $LiZnMe_2H$	2.850			2.891	2.891		2.891	2.900	
3.	$LiZnMe_2H + AlH_3$ $LiZnMe_2AlH_4$	2.791			2.783 2.791 2.850	2.775 2.783 2.850		2.816 2.833 2.900	2.766 2.800 2.850	
4.	$LiAlH_4 + Me_2Zn$ $LiZnMe_2AlH_4$	2.866 2.833 2.900			2.851 2.885 2.950	2.850 2.885 2.958		2.850 2.883 2.966	2.825 2.858 2.941	
5.	$LiAlH_4 + Me_2Zn$ $LiZnMe_2AlH_4$		4 days 2.841 br 2.833	4 days 2.791 2.891					2.858 2.916 2.966	4 weeks 2.808 2.858 2.916 2.966
6.	$LiZnMe_2H + AlH_3$ $LiZnMe_2AlH_4$		2.591 br 2.766 2.850	2.666 br 2.830 2.941					2.683 2.816	2.758 2.791
7.	$LiAlH_4 + Me_2Zn$ (-78°C) $LiZnMe_2AlH_4$				2.850 2.883 2.933	2.866 2.900 2.933			2.833 2.900	2.866 2.900 2.958
8.	$LiH + 2Me_2Zn$ $LiZn_2Me_4H$	2.766 2.755?			2.811	2.833				2.833
9.	$LiZn_2Me_4H + AlH_3$ $LiZn_2Me_4AlH_4$	2.750 2.766 2.866			2.758 2.866	2.758 2.866				2.766 2.888
10.	$LiAlH_4 + 2Me_2Zn$ $LiZn_2Me_4AlH_4$	2.816 2.858 2.866				2.841 2.866 2.925				2.850 2.888 2.925
11.	10 + 20% g	2.700			2.791 (77) 2.975 (24)					

Concerning the Existence of Complexes of $LiAlH_4$ and AlH_3 in Ether Solvents and in the Solid State

E. C. Ashby, John J. Watkins and H. S. Prasad

Abstract

The reaction between $LiAlH_4$ and AlH_3 in 1:1, 1:2, 1:3, and 1:4 molar ratios in both diethyl ether and THF has been investigated by infrared spectroscopy. Also solutions of $LiAlH_4$ and AlH_3 in diethyl ether were evaporated to dryness and the resulting solids examined by DTA-TGA and X-ray powder diffraction methods. Previous reports claiming the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ by the reaction of $LiAlH_4$ with $BeCl_2$ in ether and also the reaction of LiH with AlH_3 were studied in detail and attempts made to prepare the complexes by exactly the same procedure reported. Contrary to previous reports, in no case was any evidence found to indicate the existence of $LiAl_2H_7$, $LiAl_3H_{10}$ or any complex between $LiAlH_4$ and AlH_3 in ether or THF solution or in the solid state.

Introduction

Recently we found that diethyl ether soluble aluminum hydride can be prepared by a number of different methods.[1,2] This finding allows a convenient study of the interaction between $LiAlH_4$ and AlH_3 in diethyl ether which has been reported by a number of laboratories to be strong enough so as to produce stable complexes ($LiAlH_4 \cdot nAlH_3$, where n = 1, 2, 3 and 4). Although aluminum hydride can be prepared in tetrahydrofuran,[3]

(1) E. C. Ashby, J. P. Sanders, P. Claudy and R. D. Schwartz, Inorg. Chem., 12, 2860 (1973).

(2) E. C. Ashby, J. R. Sanders, P. Claudy and R. D. Schwartz, J. Amer. Chem. Soc., 95, 6485 (1973).

$$2\ LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2 \downarrow + 2\ AlH_3 \quad (1)$$

$$2\ LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2 \uparrow + Li_2SO_4 \downarrow + 2\ AlH_3 \quad (2)$$

$$2\ LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2\ LiCl \downarrow + ZnH_2 \downarrow + 2\ AlH_3 \quad (3)$$

(3) H. C. Brown and H. M. Yoon, J. Amer. Chem. Soc., 88, 1464, (1966).

complexes between $LiAlH_4$ and AlH_3 would not be expected to be stable due to the strong aluminum-oxygen bond in $H_3Al\text{-}OC_4H_8$.

Recent Russian work[4] claims the preparation of $LiAl_2H_7$

(4) J. N. Dymova, et al., Dokl. Akad. Nauk. SSSR, 184, 1338 (1969).

($LiAlH_4 \cdot AlH_3$) and $LiAl_3H_{10}$ ($LiAlH_4 \cdot 2AlH_3$) in diethyl ether; however, the compounds were reported to be more stable in the solid state than in ether solution. Also a recent study concerning the structure and properties of $LiAl_2H_7$ has appeared in the French literature.[5] These workers reported

(5) J. Mayet, S. Kovacevic, and J. Tranchant, Bull. Soc., Chim. France, 506, (1973).

$LiAl_2H_7$ to be stable in the solid state, but unstable in diethyl ether solution. In addition, other French workers[6] have reported the preparation

(6) J. Bousquet, J. Choury, and P. Claudy, Bull. Soc. Chim. France, 3852 (1967).

of the compound $LiAl_4H_{13}$ ($LiAlH_4 \cdot 3AlH_3$) by the reaction of LiH with AlH_3 in ether solvent. In each case the reports claim solid state stability of the complexes, but report diethyl ether solutions as being unstable.

On the other hand, several reports have appeared that claim the formation of complexes of the type $LiAlH_4 \cdot nAlH_3$ in ether solvent. It has been reported that the electrical conductivity of solutions of $LiAlH_4$ and AlH_3 in diethyl ether indicates the formation of alternate ions to those arising from $LiAlH_4$ and AlH_3 seperately.[7,8] Because of these reports

(7) Yu M. Kessler, N. M. Alpatova and O. R. Osipov, Uspekhi Khim., 33, 261 (1964).

(8) H. Noth, B.P. 820, 513 (1959).

and because of the analogy to the $MAlH_4 \cdot nAlR_3$ systems,[9] further claims for

(9) P. Kobetz, W.E. Becker, R. Pinkerton and J. B. Honeycutt, Inorg. Chem., 2, 859 (1963).

the existence of $MAlH_4 \cdot nAlH_3$ complexes have been made; in particular, $LiAl_2H_7$.[10]

(10) N. M. Alpatova, T. N. Dymova, Yu M. Kessler and O. R. Osipov, Russ. Chem. Rev., 37, 99 (1968).

We have been evaluating new hydrides as stereoselective reducing agents and felt that $LiAlH_4 \cdot AlH_3$ compounds would behave differently than either $LiAlH_4$ or AlH_3. Reduction studies in this laboratory have shown that a mixture of $LiAlH_4$ and AlH_3 in ether solvent give the same stereochemistry or reduction of 4-t-butylcyclohexanone and 3,3,5-trimethylcyclohexanone as would be expected for a simple physical mixture of $LiAlH_4$ and AlH_3. At this point we decided to take a closer look at the so called complexes "$LiAlH_4 \cdot nAlH_3$" both in ether solution by infrared spectroscopy and in the solid state by DTA-TGA and powder diffraction.

Experimental

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[11] Filtrations and other manipulations were

(11) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

carried out in a glove box equipped with a recirculating system using managanese oxide columns to remove oxygen and dry ice-acetone traps to remove solvent vapors.[12]

(12) E. C. Ashby and R. D. Schwartz, J. Chem. Ed., 51, 65 (1974).

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as nujol mulls between CsI plates. Solutions were run in matched 0.10 mm path length NaCl cells. X-ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered CuK_α radiation. Samples were sealed in 0.5 mm

capillaries and exposed to X-rays for 6 hr. d-Spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. DTA-TGA data were obtained under vacuum with a modified Mettler thermoanalyzer II. A more detailed description of this apparatus has been given elsewhere.[13,14]

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(13) E. C. Ashby and John J. Watkins, Inorg. Chem., 12, 2493 (1973).

(14) E. C. Ashby and P. Claudy, J. Chem. Ed., in press.

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[11] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration.

Materials. $LiAlH_4$ was obtained as gray, lumpy solids from Ventron, Metal Hydrides Division. Solutions of $LiAlH_4$ in diethyl ether and THF were prepared by stirring the solid hydride for 24 hours with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. Lithium hydride was prepared by the hydrogenation of t-butyl lithium at room temperature at 3000 psi for 24 hours. A slurry of LiH in diethyl ether was used. Aluminum hydride in diethyl ether was prepared by the reaction of $LiAlH_4$ with $BeCl_2$ in a 2:1 molar ratio.[1,2] The white solid was removed by filtration leaving a nearly lithium free clear solution of aluminum hydride. The molar ratios of Al, H, and Li in this solution were 1.00:3.13:0.043. Aluminum hydride in THF was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF according to the procedure of Brown.[3] Li_2SO_4 was removed by filtration and a nearly lithium free solution of AlH_3 in THF was obtained. The molar ratios of Al, H, and Li in this solution were 1.00: 3.06:0.016. These reactant solutions were standardized by aluminum analysis and transferred volumetrically. All solvents were distilled at atmospheric pressure from $LiAlH_4$ (diethyl ether) or $NaAlH_4$ (THF) immediately before use.

Reactions Involving $LiAlH_4$ and AlH_3 in Diethyl Ether. Reaction of $LiAlH_4$ and AlH_3 in 1:1, 1:2, 1:3 and 1:4 Molar Ratio. In four separate experiments, 2.5 mmoles of $LiAlH_4$ in diethyl ether was added to 2.5, 5.0, 7.5 and 10 mmoles of AlH_3 in diethyl ether. The resulting clear solutions were stirred for one hour and the infrared spectra recorded (Figure 1).

The solvent was then removed from the solution under vacuum until a dry white solid resulted. Elemental analysis of the solid products are given in Table I, the X-ray powder diffraction patterns are recorded in Table II and the vacuum DTA-TGA of the resulting solids are recorded in Figures 5, 6, 7 and 8. In all cases the infrared spectrum of the solids (Nujol mulls) yielded broad, non-distinct bands.

Reaction of $LiAlH_4$ and AlH_3 in 1:1, 1:2, 1:3 and 1:4 Molar Ratio in THF. 5 mmoles of $LiAlH_4$ in THF were added to each of the following quantities of AlH_3 in THF: (1) 5 mmoles, (2) 10 mmoles (3) 15 mmoles, and (4) 20 mmoles. In each case the resulting solutions were stirred for one hour, then the infrared spectrum recorded. The infrared spectra for these solutions are shown in Figure 2.

Reaction of LiH and AlH_3 in 1:4 Molar Ratio in Diethyl Ether. A slurry of 5 mmoles of LiH in ether was added to 20 mmoles of AlH_3 in ether. The resulting clear solution was stirred for one hour and the infrared spectrum recorded (Figure 4). The solvent was then removed from the solution under vacuum producing a dry white solid. Elemental analysis of the solid showed Li, Al, H and ether in molar ratio of 1.00:4.02:13.22:1.16. The X-ray powder diffraction patterns are recorded in Table II and the DTA-TGA of the resulting solid under argon atmosphere are recorded in Figure 12.

Reaction of $LiAlH_4$ with $BeCl_2$ in 4:1 Molar Ratio in Diethyl Ether. Twenty mmoles of $LiAlH_4$ in diethyl ether was added to 5 mmoles of $BeCl_2$ in diethyl ether. A white precipitate appeared immediately. After thirty minutes stirring the precipitate was allowed to settle. An infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 3.

Reaction of $LiAlH_4$ with $BeCl_2$ in 2:1 Molar Ratio in Diethyl Ether. Formation of "$LiAl_2H_7$". Ten mmoles of $BeCl_2$ in diethyl ether was added slowly with stirring to twenty mmoles of $LiAlH_4$ in diethyl ether cooled at -5°. A white precipitate appeared immediately. The mixture was stirred for one hour and the precipitate was allowed to settle. The infrared spectrum of the clear solution was identical with the infrared spectrum of AlH_3.

Reaction of $LiAlH_4$ with $BeCl_2$ in 3:1 Molar Ratio. Formation of "$LiAl_3H_{10}$". Fifteen mmoles of $LiAlH_4$ in diethyl ether was added to five mmoles of $BeCl_2$ in diethyl ether. A white precipitate appeared immediately. After thirty minutes stirring, the precipitate was allowed to settle. An infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 3.

Results and Discussion

The infrared spectra of $LiAlH_4$ and AlH_3 in diethyl ether and tetrahydrofuran as well as mixtures of these compounds in 1:1, 1:2, 1:3 and 1:4 ratio are shown in Figures 1 and 2. In each case the infrared spectrum of a mixture of $LiAlH_4$ and AlH_3 corresponds to a superposition of the same bands for $LiAlH_4$ and AlH_3 in the same solvent. If an actual complex between $LiAlH_4$ and AlH_3 were formed in any of the four cases studied, the infrared spectrum of the resulting solution would be expected to be different from the individual components. For example, a complex between $LiAlH_4$ and AlH_3 in solution would be expected to exhibit an Al-H-Al bridge bond. The asymmetric Al-H stretching vibration for such a bond in diethyl ether or tetrahydrofuran would be expected to occur between 1600 and 1400 cm^{-1}.[9] No such band was observed for any of the mixtures mentioned above; therefore, in diethyl ether or THF solution there is no evidence that $LiAlH_4$ and AlH_3 form complexes of the type $LiAlH_4 \cdot n(AlH_3)$ where n = 1, 2, 3 or 4.

Other workers[4-6] have reported that complexes of the type $LiAlH_4 \cdot n(AlH_3)$ are not stable in diethyl ether or tetrahydrofuran, but are stable in the solid state. In order to investigate this possibility, the same 1:1, 1:2, 1:3 and 1:4 mixtures of $LiAlH_4$ and AlH_3 in diethyl ether on which the infrared spectra were taken, were evaporated to dryness. Analysis of the resulting white solids indicated the appropriate emperical formula (Table I) ($LiAl_2H_7$, $LiAl_3H_{10}$, $LiAl_4H_{13}$, and $LiAl_5H_{16}$) which indicated the proper stoichiometric ratios and the absence of hydrolysis or ether cleavage. In each case these white solids were subjected to DTA-TGA and X-ray powder diffraction analysis.

The X-ray powder diffraction pattern for "$LiAl_2H_7$" is shown in Table II. It is readily seen that the so called complex corresponds to a mixture of $LiAlH_4$ and AlH_3. The vacuum DTA-TGA of "$LiAl_2H_7$" is shown in Figure 5. The thermogram shows gas evolution at 110, 163, 221, and 355° with simultaneous weight losses of 14.75, 1.00, 0.50, and 0.50 mg. The vacuum DTA-TGA of separate samples of $LiAlH_4$ and AlH_3 are shown in Figures 9 and 10. Aluminum hydride (Figure 10) is seen to decompose at 110° with almost simultaneous loss of both solvent and hydrogen. The first gas evolution in Figure 5 for "$LiAl_2H_7$" also occurs at 110° and its corresponding large weight loss is undoubtedly due to loss of both solvent and hydrogen. Due to large amounts of solvent loss, only the lower portion of the TGA

$$AlH_3 \rightarrow Al + 3/2\ H_2 \qquad (4)$$

is shown in Figures 5-8 so that the weight losses for the last three gas evolutions could be seen more easily. $LiAlH_4$ (Figure 9) is seen to decompose with gas evolution at 165, 224, and 410° with simultaneous weight loss in the ratio of 2:1:1. The last three gas evolutions in Figure 5 correspond

$$3\ LiAlH_4 \rightarrow Li_3AlH_6 + 2\ Al + 3\ H_2\ (165°) \qquad (5)$$

$$Li_3AlH_6 \rightarrow 3\ LiH + Al + 3/2\ H_2\ (224°) \qquad (6)$$

$$2\ LiH \rightarrow 3\ Li + 3/2\ H_2\ (410°) \qquad (7)$$

exactly with the gas evolutions in Figure 9, except for the last one; however, the ratio of the weight loss for the last three gas evolutions in Figure 5 is 2:1:1, the same as for $LiAlH_4$. When "$LiAl_2H_7$" was heated to 130° under vacuum and stoped, the X-ray powder pattern of the resulting solid showed only lines for $LiAlH_4$ and Al. The DTA-TGA for "$LiAl_2H_7$", shown in Figure 5, is readily interpreted to be due to a 1:1 mixture of $LiAlH_4$ and AlH_3. Thus, the product of solution of $LiAlH_4$ and AlH_3 is not a complex but a physical mixture.

The data indicating the composition of "$LiAl_2H_7$" as a physical mixture of AlH_3 and $LiAlH_4$ could be explained by assuming the existance of the complex $LiAl_2H_7$ which then dissociates at 110° to $LiAlH_4$ and AlH_3. However, the powder diffraction data was obtained at room temperature which shows the product "$LiAl_2H_7$" to actually be a physical mixture of $LiAlH_4$ and AlH_3. Although the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ have been reported[4] by the reaction of $LiAlH_4$ and $BeCl_2$, the infrared spectra (Figure 3) of the solutions obtained by reacting $LiAlH_4$ and $BeCl_2$ in diethyl ether in 4:1 and 3:1 mole ratios clearly shows the presence of $LiAlH_4$ and AlH_3 in the solution. The infrared spectrum of the solution obtained by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether at -5° in 2:1 mole ratio indicates the presence of only AlH_3 in solution.

$$2\ LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2\ LiCl\downarrow + 2\ AlH_3 \qquad (8)$$

$$3\ LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2\ LiCl + 2\ AlH_3 + LiAlH_4 \qquad (9)$$

$$4\ LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2\ LiCl + 2\ AlH_3 + 2\ LiAlH_4 \qquad (10)$$

The X-ray powder diffraction patterns for the proposed compounds: "$LiAl_3H_{10}$", "$LiAl_4H_{13}$", and "$LiAl_5H_{16}$" are shown in Table II. The DTA-TGA thermograms for these compounds are shown in Figures 6-8. Analogous to the reasoning used for "$LiAl_2H_7$", these compounds are also shown to be mixtures of $LiAlH_4$ and AlH_3.

We have repeated the work of Bosquet and coworkers[6] in an attempt to prepare $LiAl_4H_{13}$ by the method used in their laboratory. The infrared spectrum of the solution obtained by reaction of an ether solution of $LiAlH_4$ with an ether solution of AlH_3 is shown in Figure 4. The infrared

$$LiH + AlH_3 \xrightarrow{Et_2O} LiAl_4H_{13} \qquad (11)$$

spectrum of the solution clearly shows the presence of $LiAlH_4$ and AlH_3 in the solution. The X-ray powder pattern of the solid obtained on complete removal of solvent is shown in Table II. It is readily seen that the proposed complex closely corresponds to a mixture of $LiAlH_4$ and AlH_3. The DTA-TGA thermograms for the solids obtained by ether evaporation of the solutions formed on mixing $LiAlH_4$ and AlH_3 in diethyl ether in 1:3 mole ratio and by the reaction shown above (equation 11) are shown in Figures 12-13. The DTA-TGA of both solids are identical. Also there is a striking similarity between these thermograms and the DTA-TGA of a physical mixture of one mole of $LiAlH_4$ and three moles of $LiAlH_4$.

The X-ray powder pattern for "$LiAl_2H_7$" reported by Mayet and coworkers[5] is shown in Table I. This powder pattern resembles that of $LiAlH_4$, although no lines for AlH_3 can be detected. The "$LiAl_2H_7$" was prepared by the reaction shown in Equation 12. Unfortunately, these

$$7\ LiH + 2\ AlCl_3 \rightarrow LiAl_2H_7 + 6\ LiCl \qquad (12)$$

workers did not report any DTA-TGA or infrared spectra in their studies.

In this study, evidence has been presented to show that $LiAlH_4$ and AlH_3 do not react, under the conditions studied, to form complexes of the type $LiAlH_4 \cdot n(AlH_3)$ in either diethyl ether or THF solution. Also, evidence has been presented showing that the solids left after evaporation of the solvent from 1:1, 1:2, 1:3 and 1:4 mixtures of $LiAlH_4$ and AlH_3 in diethyl ether failed to produce complexes of the type $LiAlH_4 \cdot n(AlH_3)$. The equivalence of solutions formed by (1) addition of $LiAlH_4$ and AlH_3

in diethyl ether (2) reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether and (3) reaction of LiH and AlH_3 has been demonstrated and the solids resulting from these solutions have been shown by X-ray powder diffraction and DTA-TGA to be physical mixtures of $LiAlH_4$ and AlH_3.

Table I. Elemental Analysis of Mixtures of $LiAlH_4$ and AlH_4 in 1:1, 1:2, 1:3 and 1:4 Ratio in Diethyl Ether.

Ratio $LiAlH_4$:AlH_3	Elemental Analysis Li	Al	H	Et_2O	Mole Ratio Li : Al : H : Et_2O
1:1	7.45	56.79	7.45	28.31	1.02:2.00:7.08:0.35
1:2	4.91	55.58	6.97	32.54	1.03:3.00:10.13:0.64
1:3	3.58	53.20	6.52	36.70	1.05:4.00:13.22:1.01
1:4	2.65	51.08	6.17	40.10	1.01:5.00:16.31:1.43

Table II. X-Ray Powder Diffraction Patterns of the Solid Products Obtained in the Reactions of $LiAlH_4$ with AlH_3 in Diethyl Ether.

"$LiAl_2H_7$"[a]		"$LiAl_3H_{10}$"[b]		"$LiAl_4H_{13}$"[c]		"$LiAl_5H_{16}$"[d]		$LiAlH_4$[e]		AlH_3[f]	
d,Å	I/I_o[g]	d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o
11.4	m	11.6	m	11.6	s	11.6	s	5.36	w	11.6	vs
5.31	w	5.30	w	5.33	w	4.61	ms	4.48	m	4.59	s
4.61	mw	4.65	m	4.62	m	4.47	vw	4.00	vw	3.24	ms
4.45	m	4.41	m	4.44	w	3.87	ms	3.89	s	2.89	ms
3.85	s	3.85	s	3.85	s	3.65	vw	3.68	m		
3.67	m	3.63	m	3.66	w	3.31	w	3.53	vw		
3.41	m	3.47	m	3.45	w	3.25	s	3.43	w		
3.31	m	3.30	m	3.33	m	3.00	vw	3.32	m		
3.22	mw	3.24	m	3.24	s	2.87	ms	3.24	m		
3.00	w	3.01	w	3.01	w	2.66	vw	3.03	m		
2.92	w	2.96	w	2.95	w	2.40	vw	3.00	w		
2.85	mw	2.85	m	2.85	m			2.95	m		
2.67	w	2.65	w	2.65	w			2.68	m		
2.45	w	2.45	vw	2.45	vw			2.54	vw		
2.16	w	2.40	w	2.39	vw			2.45	w		
2.01	w	2.02	vw	2.12	vw			2.42	m		
1.78	w							2.24	w		
								2.15	w		
								2.05	w		
								2.01	vw		
								1.98	w		
								1.92	vw		
								1.89	vw		
								1.80	vw		
								1.78	w		
								1.76	w		
								1.74	w		

[a] Solid from $LiAlH_4 + AlH_3$ in 1:1 molar ratio

[b] Solid from $LiAlH_4 + AlH_3$ in 1:2 molar ratio

[c] olid from $LiAlH_4 + AlH_3$ in 1:3 molar ratio

[d] Solid from $LiAlH_4 + AlH_3$ in 1:4 molar ratio

[e] Solid from evaporating etheral $LiAlH_4$

[f] Solid from evaporating etheral $AlH_3 \cdot AlH_3$ prepared from 2:1 $BeCl_2 + LiAlH_4$

[g] s, strong; m, moderate; w, weak; v, very

Table II continued

$LiAl_2H_7$ [h]		$LiAl_4H_{13}$ [i]		$LiAl_4H_{13}$ [j]	
d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o
4.43	ms	9.450	ms	11.6	s
4.20	w	5.586	w	6.7	w
3.89	s	5.265	vw	4.55	s
3.68	vw	4.548	s	4.30	s
3.55	mw	4.439	vs	3.85	s
3.30	mw	3.045	ms	3.66	m
2.90	vww	3.888	s	3.45	m
2.65	mw	3.666	vs	3.33	w
2.588	w	3.527	w	3.02	w
2.504	m	3.456	m	2.95	m
2.376	w	3.324	w	2.85	s
2.337	vw	3.229	vs	2.65	vw
2.295	vw	3.035	ms	2.54	m
2.093	mw	2.952	vw	2.39	w
1.992	mw	2.882	vs	2.29	m
1.949	mw	2.799	vw	2.25	w
1.929	vvw	2.680	w	2.075	w
1.883	vvw	2.566	vw	1.98	vvw
1.782	vvw	2.506	vvw	1.80	w
1.765	w	2.424	w	1.69	vw
1.655	w	2.405	w	1.65	vvw
1.604	vvw	2.342	s	1.54	vw
1.572	vw	2.316	s	1.52	vw
1.558	vvw	2.271	ms	1.34	vvw
1.517	w	2.220	ms		
1.480	w	2.038	ms		
1.375	vvw	1.530	ms		
1.352	vvw	1.473	w		
1.301	vvw	1.442	w		
1.281	vvw	1.415	w		
1.194	vvw	1.344	w		

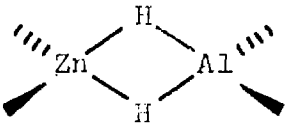
h. See reference 5. i. See reference 6.

The Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc. I. The Reaction of $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with Aluminum Hydride.

John J. Watkins and E. C. Ashby*

Abstract

When AlH_3 is allowed to react with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in tetrahydrofuran in 1:1 molar ratio, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are formed. These two compounds are the first triple metal hydride complexes involving lithium, aluminum, and zinc to be reported. An infrared spectroscopic study of these compounds in THF solution reveals that they contain the double hydrogen bridged unit:



The mechanisms of formation of these compounds by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in THF are discussed.

Introduction

Recently we have reported the synthesis of several complex metal hydrides of zinc[1-3]: Li_3ZnH_5, Li_2ZnH_4, $LiZnH_3$, Na_2ZnH_4, $NaZnH_3$,[4]

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(1) E. C. Ashby and R. G. Beach, Inorg. Chem., 10, 2486 (1971).

(2) E. C. Ashby and John Watkins, J. Chem. Soc., Chem. Comm., 998, (1972).

(3) E. C. Ashby and John J. Watkins, Inorg. Chem., 12, 2493 (1973).

(4) This compound was first prepared by Shriver and coworkers. D. J. Shriver, G. J. Kubas, and J. A. Marshall, J. Amer. Chem. Soc., 93, 5067 (1971).

$NaZn_2H_5$, K_2ZnH_4, $KZnH_3$, and KZn_2H_5. All but two of these complex metal hydrides were prepared by the reaction of $LiAlH_4$, $NaAlH_4$, or AlH_3 with an ate complex of zinc. Li_3ZnH_5, Li_2ZnH_4, and $LiZnH_3$ were prepared by the reaction of the corresponding ate complexes: $Li_3Zn(CH_3)_5$, $Li_2Zn(CH_3)_4$, and $LiZn(CH_3)_3$ with $LiAlH_4$ in diethyl ether.[2,3] $NaZnH_3$ was obtained by the reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in THF, and $KZnH_3$ was prepared by the reaction of $KZn(CH_3)_2H$ with $LiAlH_4$ in THF.[3] Quite surprisingly

$NaZn_2H_5$ and KZn_2H_5 were produced by the reaction of AlH_3 with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF.[3] Extension of the latter reaction to prepare $LiZn_2H_5$ from $LiZn(CH_3)_2H$ and AlH_3 resulted in the formation of the THF soluble complex $LiZn(CH_3)_2AlH_4$ instead. The complex $LiZn_2(CH_3)_4AlH_4$ was then prepared by reacting $LiZn_2(CH_3)_4H$ with AlH_3 in THF. $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are the first triple metal hydride complexes involving an alkali metal, zinc, and aluminum to be reported.

Since our discovery of the use of aluminohydrides in the synthesis of main group complex metal hydrides,[2,3] we have been very interested in the nature of exchange reactions between Al-H species and main group alkyl metal species. We feel that, in addition to providing a route to triple metal hydrides, an indepth study of the formation of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ could provide insight into the nature of exchange reactions between $LiAlH_4$, $NaAlH_4$, or AlH_3 and the ate complexes of zinc. It is the purpose of this paper to provide a foundation for the detailed understanding of the above transformations.

Experimental

Apparatus. Reactions were performed under nitrogen using Schlenk tube techniques.[5] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system.[6]

(5) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(6) E. C. Ashby and R. D. Schwartz, J. Chem. Ed., 51, 65 (1974).

Infrared spectra were obtained using a Perkin Elmer 621 Spectrophotometer. Solutions were run in matched 0.10 mm pathlength NaCl cells. X-ray powder data were obtained on a Phillips-Norelco X-ray unit with a 114.6 mm camera with nickel filtered CuK_α radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hours. d-Spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually.

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Methane in the presence of hydrogen was determined in a tensimeter.

Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc in the absence of other metals was determined by EDTA titration.

Materials. Lithium hydride was prepared by hydrogenolysis of t-butyllithium at 4000 psi for 24 hours. Dimethylzinc was prepared by the procedure of Noller.[7] Methyl iodide was obtained from Fisher Scientific.

(7) C. R. Noller, Org. Syn., 12, 86 (1932).

The iodide was dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc-copper couple was obtained from Alfa Inorganics. The reaction of zinc-copper couple with methyl iodide was allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture under nitrogen. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$. Ultra-pure hydrogen (99.9995%) obtained from the Matheson Corporation was used for hydrogenation experiments. Aluminum hydride was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration resulting in a clear and colorless solution of AlH_3 in THF.[8]

(8) H. C. Brown and H. M. Yoon, J. Amer. Chem. Soc., 88, 1464 (1966).

Reaction of AlH_3 with $LiZn(CH_3)_2H$ in Tetrahydrofuran. Five mmoles of dimethylzinc in tetrahydrofuran were added to 5 mmoles of a lithium hydride slurry in tetrahydrofuran. This mixture was stirred until all the lithium hydride dissolved (forming $LiZn(CH_3)_2H$), then 5 mmoles of AlH_3 in THF were added. After one hour stirring no precipitate was visable. An infrared spectrum was obtained on the clear solution. The spectrum is shown in Figure 1 along with the spectra of $(CH_3)_2Zn$, AlH_3, and $LiZn(CH_3)_2H$ in THF. The infrared spectrum of the solution does not correspond to a mixture of AlH_3 and $LiZn(CH_3)_2H$. After a few hours at room temperature a black solid began to precipitate. Precipitation continued over a long period of time.

Samples of the product from the reaction of $LiZn(CH_3)_2H$ with AlH_3 were prepared for a stability study. Infrared spectra were obtained on the supernatent solution at periods of 1 hour, 5 hours, 24 hours, 2 days, 4 days, 7 days, 2 weeks, and 3 weeks after the initial mixing of the reactants.

In every case the infrared spectrum of the supernatent solution was the same as that shown in Figure 1, except the spectra became less intense with time. A black solid was present in the flask during the entire three week period, except for the first four hours. At the end of the three week period the supernatent solution contained a little less than one half the starting zinc (2.47 mmoles of the starting 5 mmoles of zinc). The black solid present at the end of the three week period was separated by filtration, washed with THF, and dried under vacuum overnight at room temperature. Analysis of the black solid revealed that it contained Li:Zn:H:Al in molar ratios of 1.06:2.00:1.93:0.07. An X-ray powder diffraction pattern of the black solid contained lines due to $LiZnH_3$ and Zn metal only.

In a separate experiment, $LiZn(CH_3)_2H$ and AlH_3 were allowed to react and sit at room temperature for one week. At the end of this one week time period the black solid, which had formed, was separated by filtration, washed with THF, and dried under vacuum at room temperature overnight. Analysis of the black solid revealed that it contained Li:Zn:H:Al in molar ratios of 1.04:2.00:3.28:0.04. An X-ray powder diffraction pattern of the black solid contained lines due to $LiZnH_3$ and Zn metal only.

Attempts were made to obtain the compound formed by reacting $LiZn(CH_3)_2H$ with AlH_3 as a solid by stripping off the THF solvent at room temperature because of our interest in obtaining X-ray powder diffraction and DTA-TGA analysis on the solid. However, these attempts always gave a black, gummy material which was unsuitable for use. An attempt was made to seperate the compound as a solid by crystallization at reduced temperature; but no crystals formed. The solution of this compound in THF stayed clear and did not precipitate any black solid for indefinite periods of time when cooled to Dry Ice acetone temperature. An attempt to obtain the solid compound by stripping THF from solution at reduced temperatures resulted in a gum which turned black on warming to room temperature.

Reaction of AlH_3 with $LiZn_2(CH_3)_4$ in Tetrahydrofuran. Dimethylzinc in tetrahydrofuran (8.35 mmoles) was added to 4.18 mmoles of LiH slurried in THF. A clear solution resulted to which was added 4.17 mmoles of AlH_3 in THF. The mixture remained clear even after one hour stirring. At this time an infrared spectrum of the solution was obtained. The spectrum is

shown in Figure 2 along with the infrared spectra of $(CH_3)_2Zn$, AlH_3 and $LiZn_2(CH_3)_4H$ in THF. The infrared spectrum of the solution does not correspond to a mixture of AlH_3 and $LiZn_2(CH_3)_4H$.

As in the case of the product of $LiZn(CH_3)_2H$ and AlH_3 in THF, the product of the reaction of $LiZn_2(CH_3)_4H$ and AlH_3 in THF also began to precipitate a black solid on standing at room temperature. However, the latter solution stood overnight before any black solid was observed. A stability study, similar to the one carried out on the product from the reaction of $LiZn(CH_3)_2H$ with AlH_3 was carried out on a THF solution of the product from the reaction of $LiZn_2(CH_3)_4H$ with AlH_3. The results were similar. After sitting three weeks, an infrared spectrum of the supernatent solution was the same as that for the product shown in Figure 2, only less intense. The black solid that separated was found to be a mixture of $LiZnH_3$ and zinc metal. As with the reaction of $LiZn(CH_3)_2H$ with AlH_3, attempts to obtain a solid sample of the product from the reaction of $LiZn_2(CH_3)_4H$ with AlH_3 for X-ray powder diffraction and DTA-TGA analysis were futile.

Results and Discussion

When AlH_3 was allowed to react with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF, $NaZn_2H_5$ and KZn_2H_5 were formed according to equations 1 and 2. On the other hand, when AlH_3 was allowed to react with $LiZn(CH_3)_2H$ a reaction similar to these was not observed. The reaction yielded no precipitate,

$$2\ NaZn(CH_3)_2H + 2\ AlH_3 \rightarrow NaZn_2H_5 \downarrow + NaAl_2(CH_3)_4H_3 \qquad (1)$$

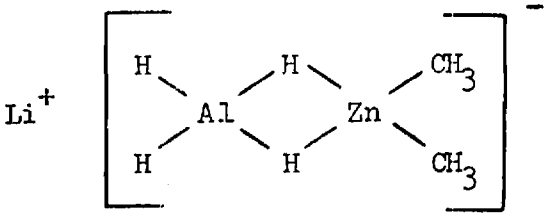
$$2\ KZn(CH_3)_2H + 2\ AlH_3 \rightarrow KZn_2H_5 \downarrow + KAl_2(CH_3)_4H_3 \qquad (2)$$

only a clear solution. This behavior shows that $LiZn_2H_5$ was not formed since this compound would be expected to be insoluble in THF. Information concerning the nature of the species present in solution can be obtained by examining the infrared spectrum of the reaction solution (Figure 1). The infrared spectrum of the reaction mixture does not correspond to a mixture of the starting materials, indicating that some type of reaction has taken place. There is a strong broad band in the terminal Al-H stretching region centered at 1660 cm^{-1} and another broad band in the metal-H stretching region centered at 1400 cm^{-1}. The terminal Al-H stretching vibration for AlH_3 and $LiAlH_4$ in THF occurs at 1740 and 1691 cm^{-1}, respectively. Neither of these abosrptions correspond to the observed

band. The Al-H stretching vibration for $LiAl(CH_3)_2H_2$ in THF occurs at approximately 1660 cm^{-1}. However, in order for $LiAl(CH_3)_2H_2$ to be present in solution, methyl-hydrogen exchange as well as alkali metal exchange between $LiZn(CH_3)_2H$ and AlH_3 would have had to occur. This reaction, shown in equation 3, would have resulted in the precipitation of ZnH_2. Since no

$$LiZn(CH_3)_2H + AlH_3 \not\rightarrow LiAl(CH_3)_2H_2 + ZnH_2 \qquad (3)$$

precipitate was observed and since the Zn-CH_3 stretching vibration at 690 cm^{-1} was still present in the spectrum of the product, the presence of $LiAl(CH_3)_2H_2$ is doubtful. A reasonable suggestion at this point is that $LiZn(CH_3)_2H$ and AlH_3 form the stable complex, $LiZn(CH_3)_2AlH_4$. A tentative



$[LiZn(CH_3)_2AlH_4]$

structure is shown here and the following discussion will attempt to establish the reasonabliness of this suggestion.

The reaction of $LiZn_2(CH_3)_4H$ with AlH_3, like the reaction of $LiZn(CH_3)_2H$ with AlH_3, yielded a clear solution. The infrared spectrum of the reaction mixture (Figure 2) did not contain any bands in the terminal Al-H stretching region (1900-1600 cm^{-1}), only a broad peak centered at 1400 cm^{-1}. (This same band was observed in the infrared spectrum of $LiZn(CH_3)_2AlH_4$). Also there is no terminal Al-H deformation band in its characteristic region (800-700 cm^{-1}); however, there is a Zn-CH_3 stretching band at 700 cm^{-1}. The infrared spectrum of the reaction mixture does not correspond to a mixture of the starting materials, indicating again that some type of reaction has taken place. Any set of products that are proposed to be formed by the reaction of $LiZn_2(CH_3)_4H$ with AlH_3 must fulfill the following set of conditions, which are derived from this infrared spectrum and the physical appearance of the product solution.

The conditions are as follows: (1) The products must be soluble, no precipitate can be formed; (2) The products cannot exhibit a terminal Al-H band; (3) The products must contain a Zn-CH_3 bond; (4) Whatever product is proposed to give rise to the infrared band at 1400 cm^{-1} must be consistent with the product from the reaction of $LiZn(CH_3)_2H$ with AlH_3, since the same band is observed there. The consideration of ZnH_2, $LiZnH_3$, and $LiZn_2H_5$ as possible products can be ruled out on the basis of condition 1. This leads to the consideration of reactions to form soluble products. Possible reaction pathways to give soluble products are shown in equations 4-7.

$$LiZn_2(CH_3)_4H + AlH_3 \rightarrow \begin{cases} 2\ CH_3ZnH + LiAl(CH_3)_2H_2 & (4) \\ LiZn_2(CH_3)_3H_2 + CH_3AlH_2 & (5) \\ LiZn_2(CH_3)_2H_3 + (CH_3)_2AlH & (6) \\ LiZn_2(CH_3)H_4 + (CH_3)_3Al & (7) \end{cases}$$

The products from each of these reactions satisfy conditions 1 and 3; but only the products of equation 7 satisfy condition 2. Therefore, the reactions shown in equations 4-7 don't take place. The products of equation 7 fulfill the first three conditions; however, the fulfillment of condition 4 needs to be discussed.

In order to consider condition 4, one can assume that the band at 1400 cm^{-1} in the infrared spectrum of the products from the reaction of $LiZn_2(CH_3)_4H$ with AlH_3 is due to $LiZn_2(CH_3)H_4$. If this is so, then the band at 1400 cm^{-1} in the infrared spectrum of the products from the reaction of $LiZn(CH_3)_2H$ with AlH_3 must also be due to $LiZn_2(CH_3)H_4$. The reaction between $LiZn(CH_3)_2H$ and AlH_3 to form $LiZn_2(CH_3)H_4$ would have to proceed as shown in equation 8. Now if equation 8 describes the reaction, the infrared

$$LiZn(CH_3)_2H + AlH_3 \rightarrow 1/2\ LiZn_2(CH_3)H_4 + 1/2\ "LiAl_2(CH_3)_3H_4" \quad (8)$$

spectrum of the compound "$LiAl_2(CH_3)_3H_4$" prepared independently should match the infrared spectrum of the products from the reaction of $LiZn(CH_3)_2H$ with AlH_3 in the 1800-1500 cm^{-1} region (Figure 3). The compound of imperical formula "$LiAl_2(CH_3)_3H_4$" could be a complex or a 2:1:1 mixture of $(CH_3)_2AlH$: $LiAlH_4$:$LiAl(CH_3)_2H_2$. Whether it is a complex or a mixture, the infrared spectrum of the 2:1:1 mixture should be identical to the reaction product of

$LiZn(CH_3)_2H$ and AlH_3 in the 1800-1500 cm^{-1} region, if indeed one of the products of this reaction is $LiAl_2(CH_3)_3H_4$. The infrared spectrum of a 2:1:1 mixture of $(CH_3)_2AlH$, $LiAlH_4$, and $LiAl(CH_3)_2H_2$ in THF is shown in Figure 4. The 2000-1500 cm^{-1} region of the spectrum contains a broad band extending from 1900 to 1500 cm^{-1}. This band is centered at about 1680 cm^{-1} and has a shoulder at 1750 cm^{-1}. The shoulder at 1750 cm^{-1} is due to $(CH_3)_2AlH$. The infrared spectrum of the compound "$LiAl_2(CH_3)_3H_4$" in the 1800-1500 cm^{-1} region does not match the infrared spectrum of the products from the reaction of $LiZn(CH_3)_2H$ with AlH_3 in this region. Therefore, the reaction as written in equation 8 cannot be correct and the band at 1400 cm^{-1} in the product mixture from the reactions of $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with AlH_3 cannot be due to $LiZn_2(CH_3)H_4$. This shows that the products of equation 7 do not satisfy condition 4 and the reaction as written in equation 7 does not take place.

Shriver and coworkers[9] have suggested the following two structures

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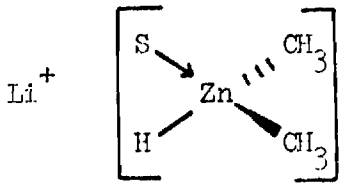
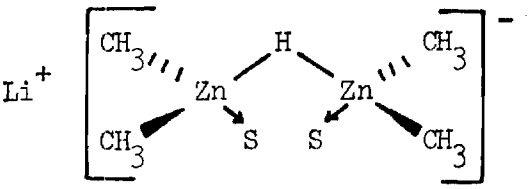
(9) G. J. Kubas and D. F. Shriver, J. Amer. Chem. Soc., 92, 1949, (1970).



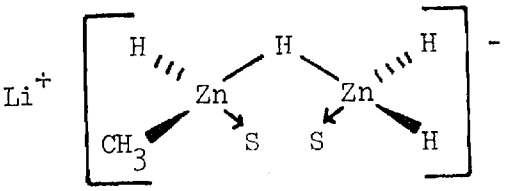
$LiZn(CH_3)_2H$



$LiZn_2(CH_3)_4H$

for $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$. Referring to the data generated in this study (Table 1) one can see that the Zn-H stretching frequency for $LiZn_2(CH_3)_4H$ is lower than that for $LiZn(CH_3)_2H$. These data are consistent with the structures suggested by Shriver and coworkers since one would expect the bridging Zn-H-Zn band in the $LiZn_2(CH_3)_4H$ to have a lower stretching frequency than the non-bridging Zn-H band in $LiZn(CH_3)_2H$. It is interesting to note that the Zn-H stretching band reported by Shriver and coworkers[9] for desolvated $LiZn(C_6H_5)_2H$ in Nujol mull occurred as a broad peak extending from 1250-1650 cm^{-1}. The band reported in this work for the Zn-H stretching modes of $LiZn(CH_3)_2H$ in THF (Figure 3) also extend from 1250-1650 cm^{-1} with the center at 1450 cm^{-1}. Since both zinc atoms in

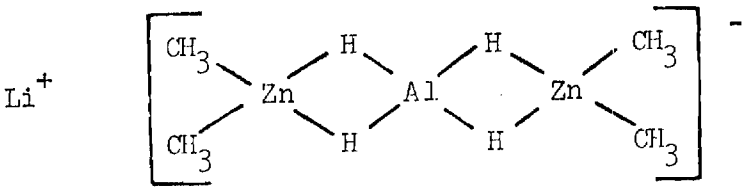
$LiZn_2(CH_3)_4H$ are joined by a hydride bridge bond, it seems reasonable that both zinc atoms in the compound $LiZn_2(CH_3)H_4$ would also be joined by a hydride bridge bond. The complex $LiZn_2(CH_3)H_4$ would then have the structure shown below. This compound would contain three types of Zn-H bonds: two



$LiZn_2(CH_3)H_4$

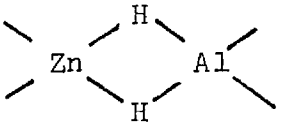
different types of terminal Zn-H bonds and one bridging Zn-H-Zn bond. These three different types of Zn-H bonds should give rise to three Zn-H stretching bands in the infrared. The bands for the two types of terminal Zn-H bonds should be very close to one another, both of them being centered between 1500 and 1450 cm^{-1}. The band for the bridging Zn-H-Zn bond should be centered at about 1300 cm^{-1}. Although the two terminal Zn-H bands may not be separated (due to the broad nature of Zn-H stretching bands), the terminal Zn-H and the bridging Zn-H-Zn bands would be far enough apart for one to be able to distinguish them. Referring to Figure 3, one sees only one band in the 1800-1200 cm^{-1} region of the infrared spectrum for the product of the reaction between $LiZn_2(CH_3)_4H$ and AlH_3. This band is centered at 1400 cm^{-1} and is not as broad as the Zn-H stretching bands observed for $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$. It is more narrow, like the Al-H stretching bands (see the infrared spectrum for AlH_3 shown in Figure 3). This evidence indicates that the band at 1400 cm^{-1} cannot be due to $LiZn(CH_3)H_4$ and offers additional evidence for overruling the reaction as written in equation 7. However, the similarity in shape between the band at 1400 cm^{-1} and the Al-H stretching band of AlH_3 indicates that the compound which give rise to the band at 1400 cm^{-1} contains some type of Al-H bond.

The most reasonable description of the reaction product formed on addition of $LiZn_2(CH_3)_4H$ to AlH_3 is that of a stable complex between the two components. The proposed structure of this complex is shown below. In view of the fact that there are no terminal aluminum hydrogen bands in the



$[LiZn_2(CH_3)_4AlH_4]$

infrared spectrum of the complex, this is the only reasonable structure that can be drawn. The broad band centered at 1400 cm^{-1} is in the right region for Zn-H stretching modes and bridging Al-H stretching modes. Therefore, this band is assigned to the metal hydride stretching modes for the group:



This band at 1400 cm^{-1} was also observed in the infrared spectrum of $LiZn(CH_3)_2AlH_4$; therefore, $LiZn(CH_3)_2AlH_4$ should contain the bridged unit shown above. The tentative structure proposed earlier for $LiZn(CH_3)_2AlH_4$ is consistent with the structure proposed for $LiZn_2(CH_3)_4AlH_4$.

The infrared bands for $(CH_3)_2Zn$, AlH_3, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, $LiZn(CH_3)_2AlH_4$, and $LiZn_2(CH_3)_4AlH_4$ are given in Table 1. It is interesting to note certain trends and differences among the compounds listed in this Table. For a given metal, a decrease in the symmetric methyl deformation frequency indicates less covalent bonding between the methyl group and the metal.[10] The symmetric methyl deformation band shifts from 1153 cm^{-1} for

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(10) M. Tsutsui, "Characterization of Organometallic Compounds," Part I, p. 75, Interscience Publishers, 1969.

$(CH_3)_2Zn$ to 1118 cm^{-1} for $LiZn(CH_3)_2H$, indicating that there is less $Zn-CH_3$ covalent bonding in $LiZn(CH_3)_2H$ than in $(CH_3)_2Zn$. This result would have been predicted on the basis of the expected greater ionic character of the $Zn-CH_3$ bond in $LiZn(CH_3)_2H$ as compared to $(CH_3)_2Zn$. The methyl rocking frequency also decreased on formation of the complex $LiZn(CH_3)_2H$ from $(CH_3)_2Zn$. The Zn-C stretching mode increased in frequency in the order: $(CH_3)_2Zn$ (674 cm^{-1}) < $LiZn(CH_3)_2H$ (680 cm^{-1}) < $LiZn(CH_3)_2AlH_4$ (690 cm^{-1}). On going from $(CH_3)_2Zn$ to $LiZn_2(CH_3)_4H$ to $LiZn_2(CH_3)_4AlH_4$, the $Zn-CH_3$ stretching frequency goes from 674 to 668 to a rather high value of 700 cm^{-1}. Considering the methyl deformation frequencies, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, and $LiZn(CH_3)_2AlH_4$ appear to have approximately the same degree of $Zn-CH_3$ ionic character, while $LiZn_2(CH_3)_4AlH_4$ appears to have more covalent character.

The mechanism of formation of $LiZn(CH_3)_2AlH_4$ by the reaction of $LiZn(CH_3)_2H$ with AlH_3 can be visualized as occuring in the manner shown

in Scheme I. Aluminum hydride, which is known to be in four coordinate-five coordinate equilibrium in THF,[11] reacts as the four coordinate species.

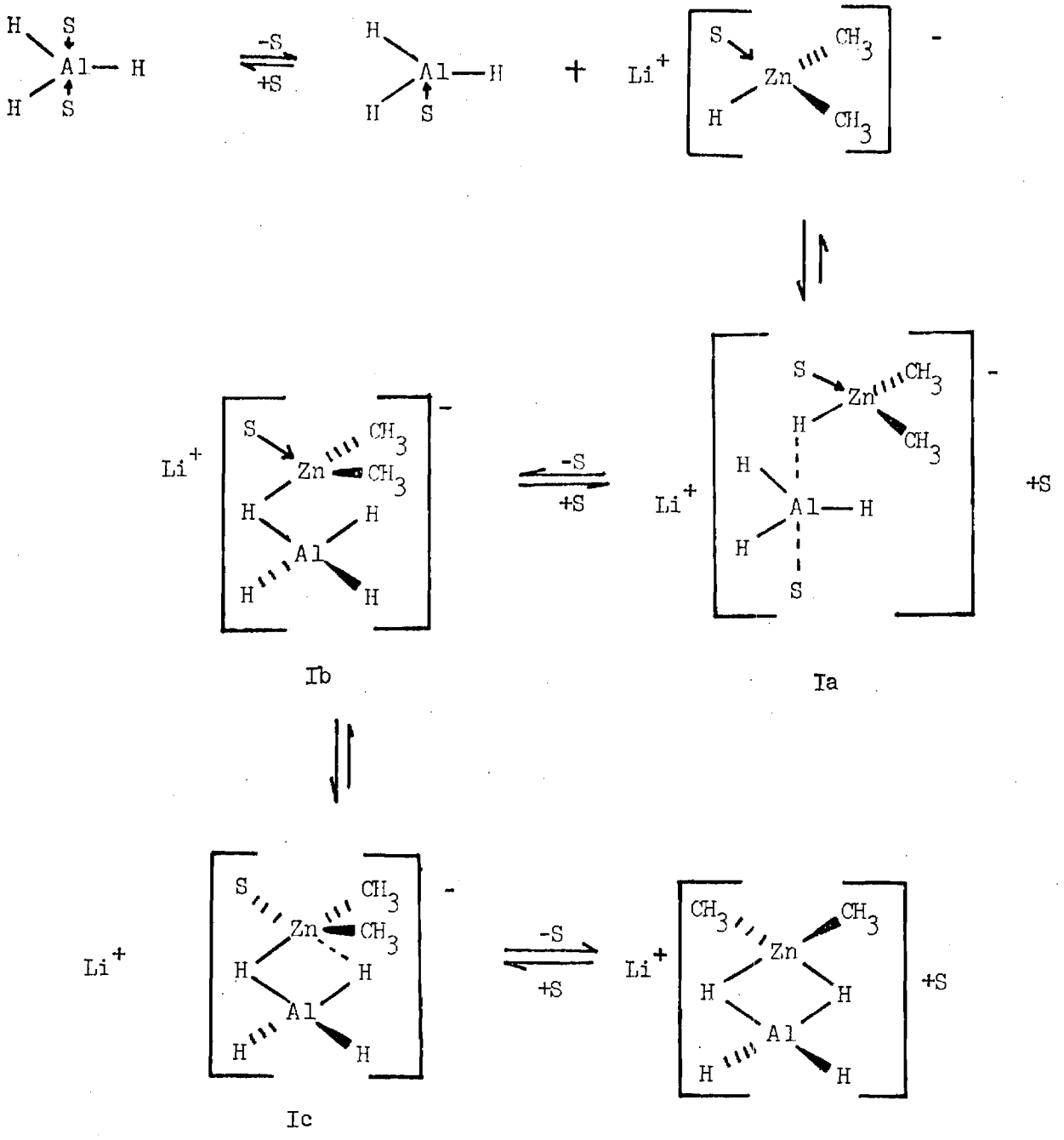
(11) R. Dautel and W. Zeil, Zeit. Elektrochem., 62, 1139, (1958).

The four coordinate alane species undergoes nucleophilic attack by $LiZn(CH_3)_2H$ to yield the intermediate Ib via transition state Ia. The result of this nucleophilic solvent displacement is the formation of a three-center Al-H-Zn bond. The intermediate Ib then undergoes an intramolecular nucleophilic displacement by hydrogen on the zinc atom to displace the coordinated solvent molecule. This reaction occurs thru the transition state Ic to form $LiZn(CH_3)_2AlH_4$. All the steps shown are suggested to be reversible; however, the equilibrium lies predominantly toward $LiZn(CH_3)_2AlH_4$, since it is the only species observed in the infrared spectrum when AlH_3 and $LiZn(CH_3)_2H$ are allowed to react.

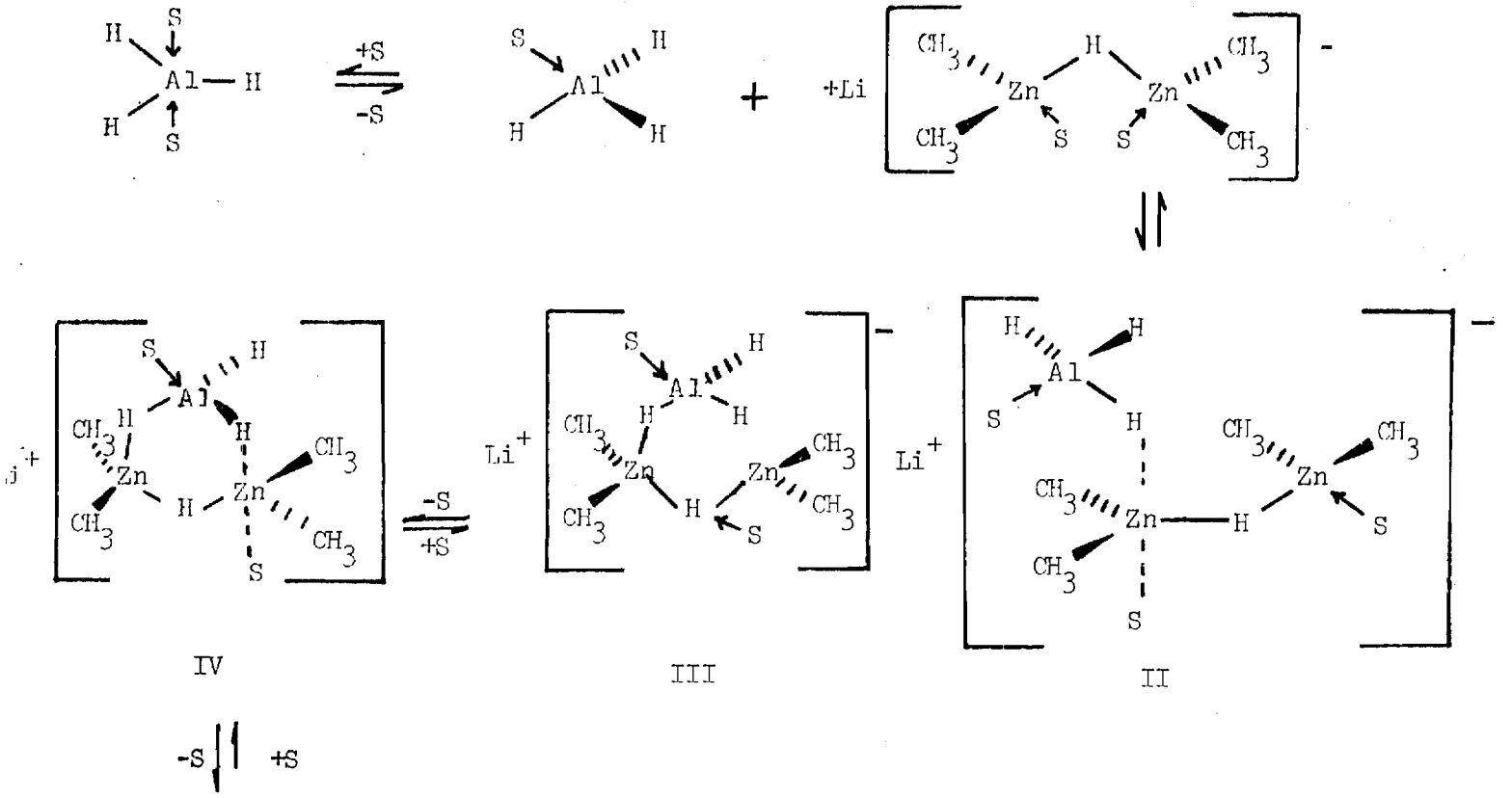
The mechanism of formation of $LiZn_2(CH_3)_4AlH_4$ by reaction of AlH_3 with $LiZn_2(CH_3)_4H$ can be visualized as occuring in the manner shown in Scheme II. Just as in the previous mechanism, the very first step involves the loss of solvent in five coordinate alane to form four coordinate alane. The four coordinate alane then reacts with $LiZn_2(CH_3)_4H$ to give intermediate III via transition state II. Intermediate V is then formed via transition state IV. The Zn-H-Zn bridge bond in V is then cleaved by reaction with solvent via transition state VI to form intermediate VII. Intermediate VII then undergoes the loss of solvent from zinc and aluminum via transition states VIII and X, respectively, to form the final product XI. Again, the equilibrium lies largely in favor of $LiZn_2(CH_3)_4AlH_4$, since it is the only species observed in the infrared spectrum. The critical step in this mechanism is the attack of a solvent molecule on V to give VII. If the Zn-H-Zn bridge bond in V is strong enough that it cannot be broken by solvent attack on zinc, then only a compound such as V will be formed and it will not be able to react further to give a compound with the same structure as $LiZn_2(CH_3)_4AlH_4$. This is the case when AlH_3 reacts with $KZn_2(CH_3)_4H$.[12]

(12) John J. Watkins and E. C. Ashby (manuscript in preparation)

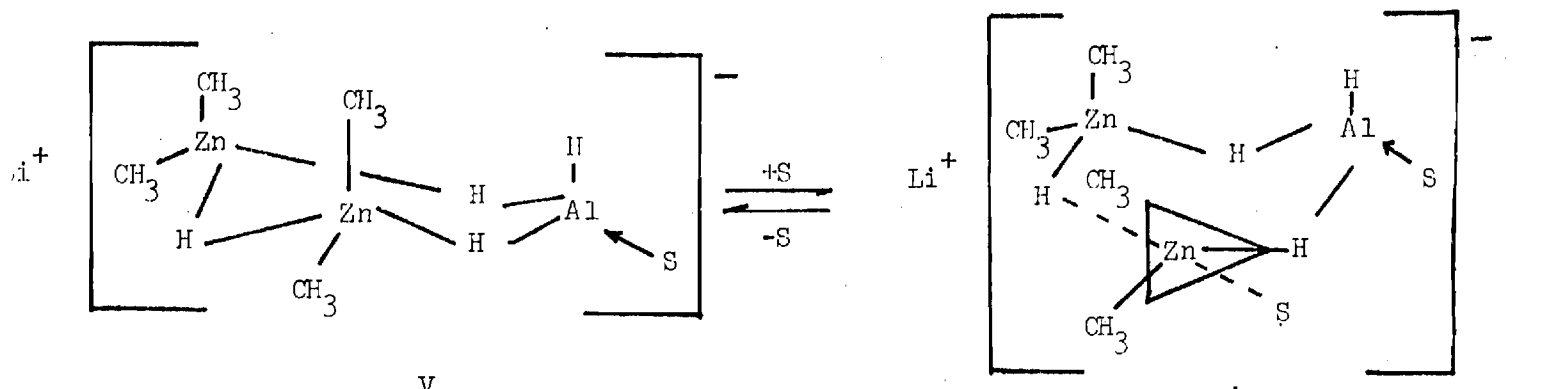
SCHEME I



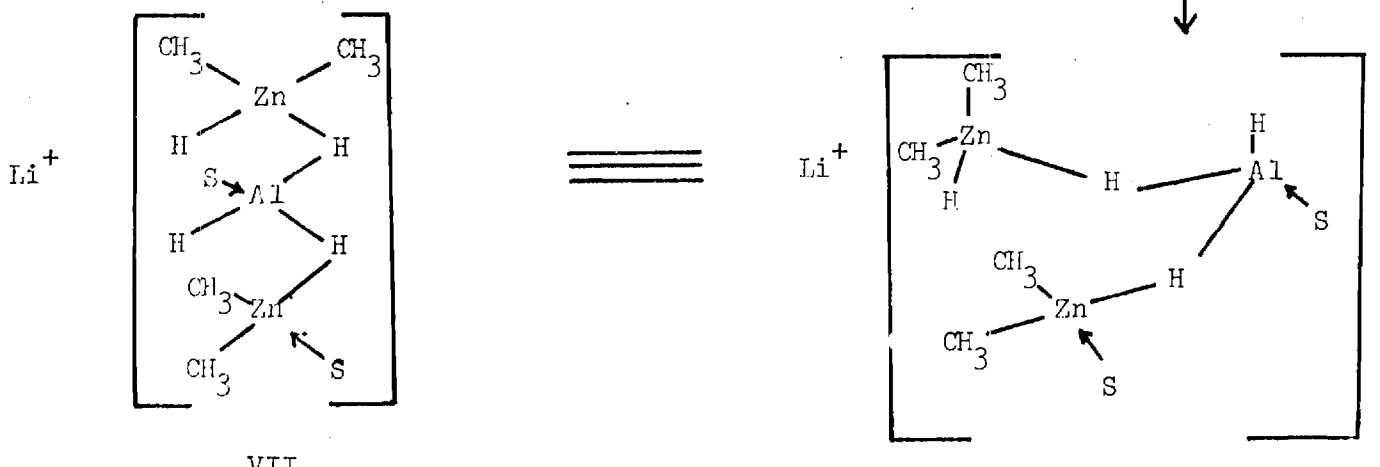
SCHEME II



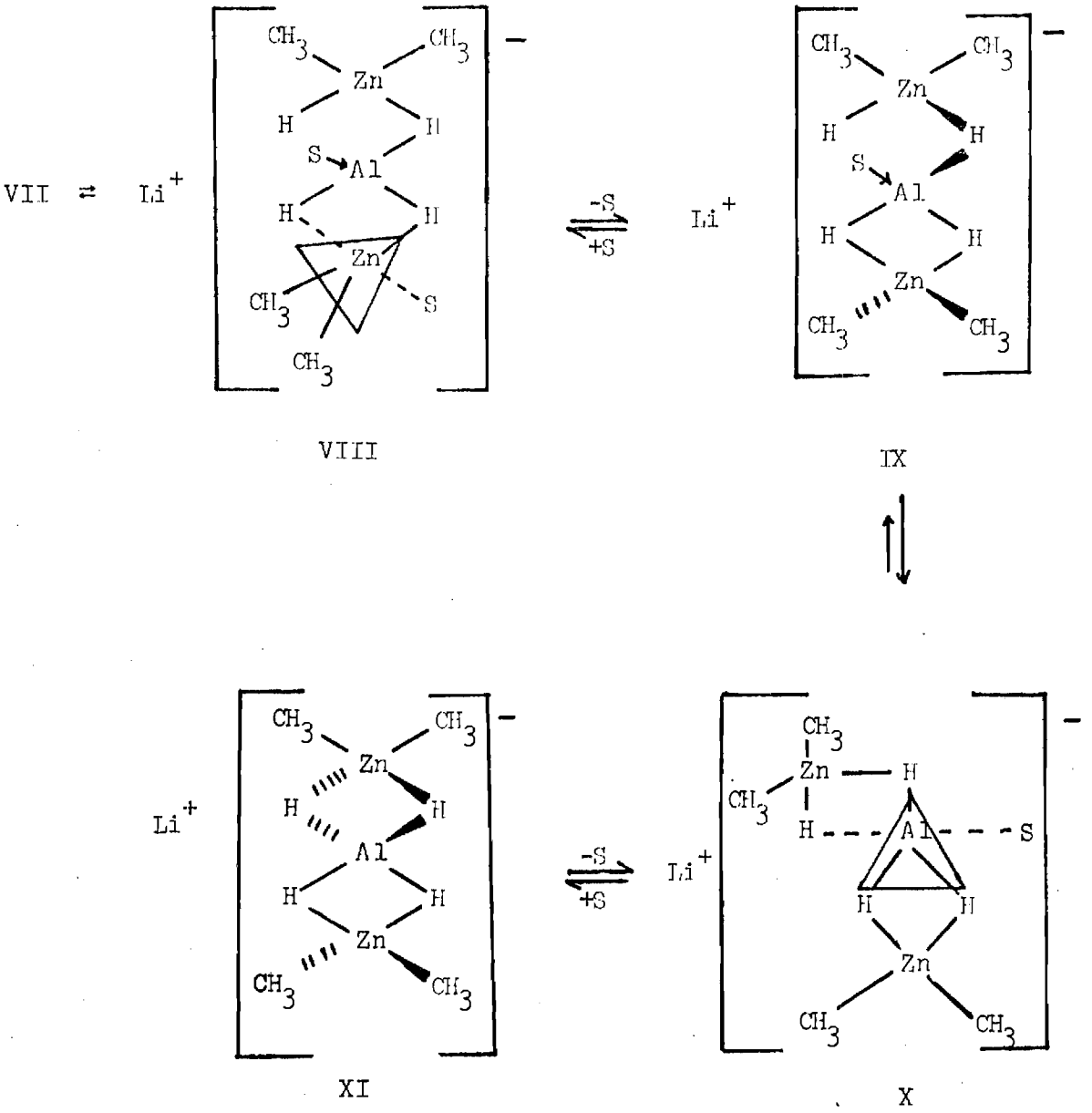
IV III II



V VI



VII VII


VII ⇄ Li+
CH3
Zn
H
S
Al
-S
+S
VIII
IX
Li+
XI
X

A discussion of why a solid with a Li:Zn ratio of 1:2 forms when $LiZn(CH_3)_2AlH_4$ is allowed to stand at room temperature will be more appropriately included in a later paper[12] dealing with the mechanisms of the reactions of $NaZn(CH_3)_2H$ and $NaZn_2(CH_3)_4H$ with AlH_3 in THF. The mechanisms of the reactions of $KZn(CH_3)_2H$ and $KZn_2(CH_3)_4H$ with AlH_3 to produce KZn_2H_5 will also be discussed at that time.

The discovery of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ provides some insight into the nature of alkyl-hydrogen exchange reactions between zinc and aluminum. For example, the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in diethyl ether is a standard method for the preparation of zinc hydride.[13] One

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(13) G. D. Barbaras, C. Dillard, A. E. Finholt, J. Wartik, K. E. Wilzbach, and H. D. Schlesinger, J. Amer. Chem. Soc., 73, 4858 (1951).

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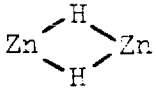
would expect this reaction to involve an intermediate such as $LiZn(CH_3)_2AlH_4$. An infrared spectral study of the reaction of $(CH_3)_2Zn$ and $LiAlH_4$ in THF does provide evidence concerning this point.[12]

Acknowledgement. We are indebted to the Office of Naval Research Contract Authority

Table 1. Infrared Spectral Bands for $(CH_3)_2Zn$, AlH_3, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, $LiZn(CH_3)_2AlH_4$, and $LiZn_2(CH_3)_4AlH_4$ in THF.[a]

OBSD IR BANDS, CM^{-1}[b]						Approximate Assignment
$(CH_3)_2Zn$	AlH_3	$LiZn(CH_3)_2H$	$LiZn_2(CH_3)_4H$	$LiZn(CH_3)_2AlH_4$	$LiZn_2(CH_3)_4AlH_4$	
674 vs		680 vs	668 vs	690 vs	700 vs	Zn-C stretch
	728 vs 755 w 795 s			720 sh, s 775 s		Al-H deformation
840 m		795 w				CH_3 rock
1153 m		1118 m	1120 m	1118 m	1140 m	CH_3 deformation
				1162 m	1170 w	?
		1450 br,[c] s	1290 br,[c] s			Zn-H stretch
				1400 br,[c] s	1400 br,[c] s	
	1740 vs			1660 br,[c] vs		terminal Al-H stretch

a. All spectra were run with THF as reference; b. Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; v, very; br, broad; c. These bands were broad. The frequency given is approximately the center of the band.

Figure 1. Infrared Spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn(CH_3)_2H$ in THF, (d) $LiZn(CH_3)_2AlH_4$ in THF.

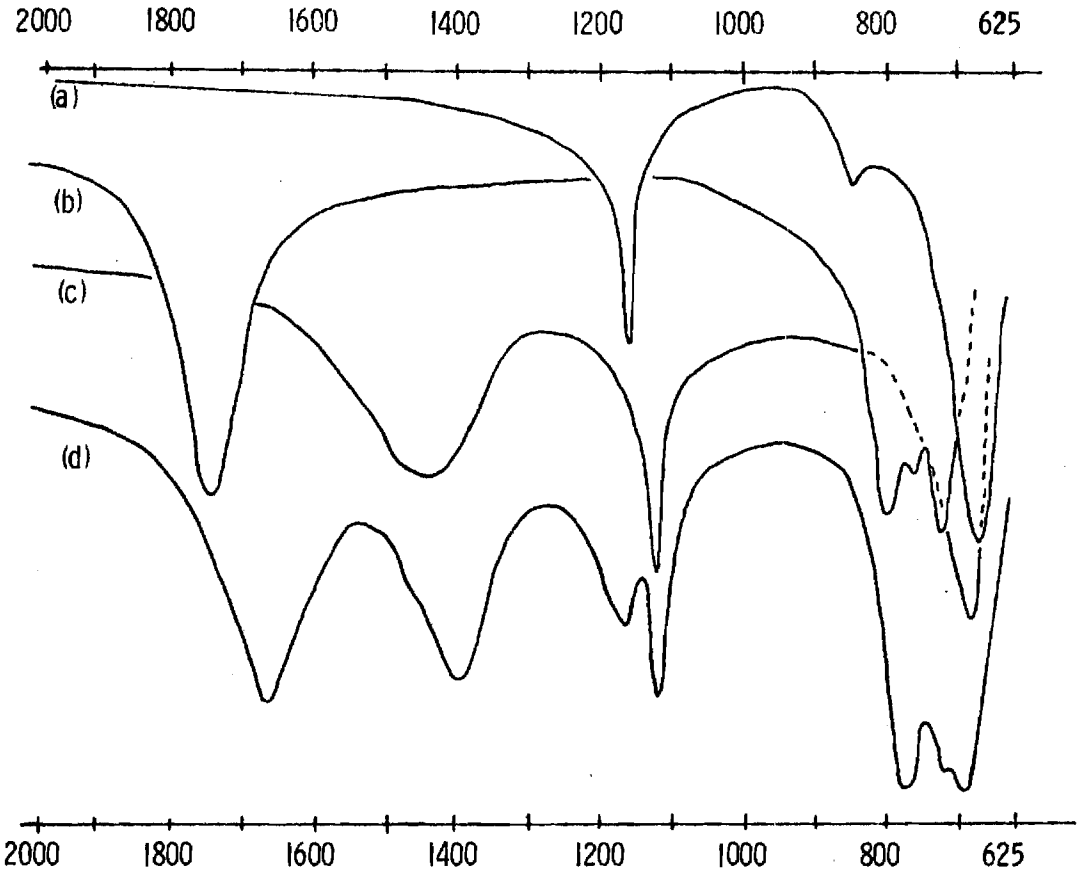
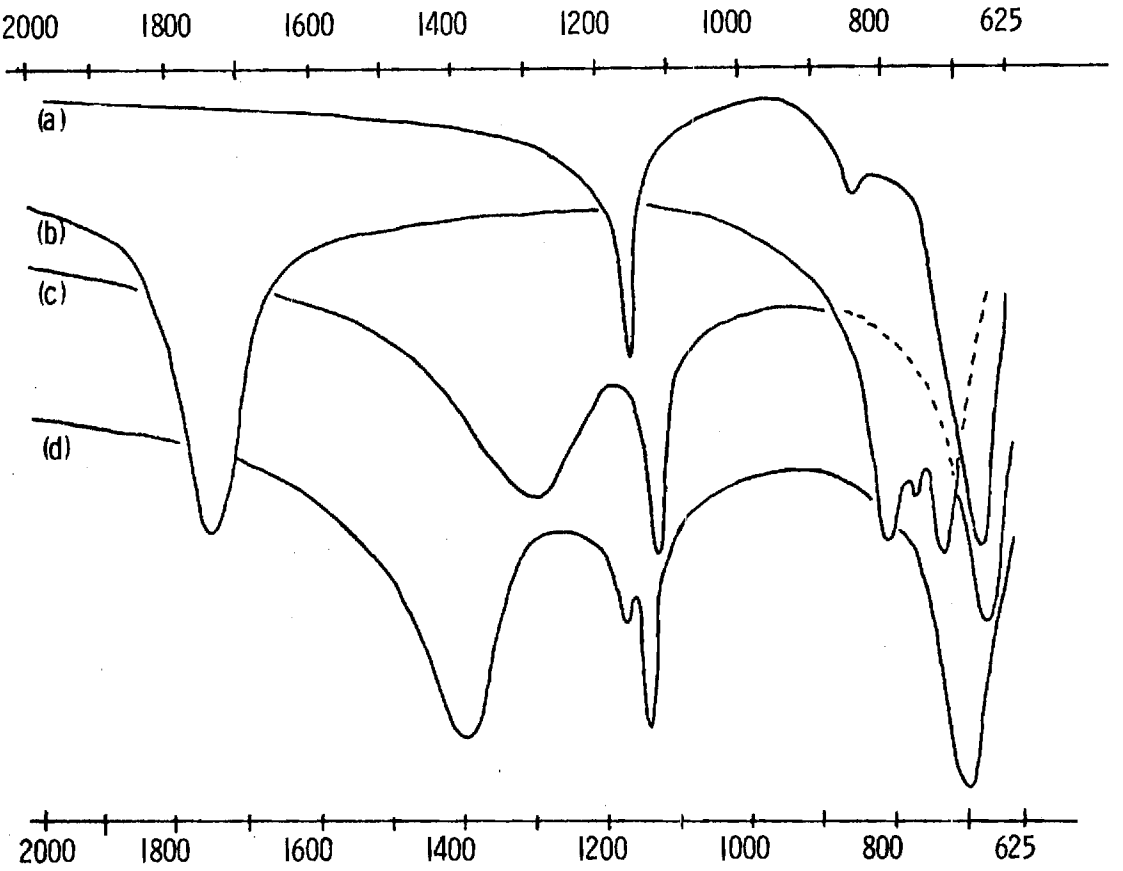

2000
1800
1600
1400
1200
1000
800
625
(a)
(b)
(c)
(d)
2000
1800
1600
1400
1200
1000
800
625

Figure 2. Infrared Spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn_2(CH_3)_4H$ in THF, (d) $LiZn_2(CH_3)_4AlH_4$ in THF.


2000
1800
1600
1400
1200
1000
800
625
(a)
(b)
(c)
(d)
2000
1800
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1400
1200
1000
800
625

Figure 3. 1800-1200 cm^{-1} Region of the Infrared Spectrum for (a) AlH_3 in THF, (b) $LiZn(CH_3)_2H$ in THF, (c) $LiZn(CH_3)_2AlH_4$ in THF, (d) $LiZn_2(CH_3)_4H$ in THF, (e) $LiZn_2(CH_3)_4AlH_4$ in THF.

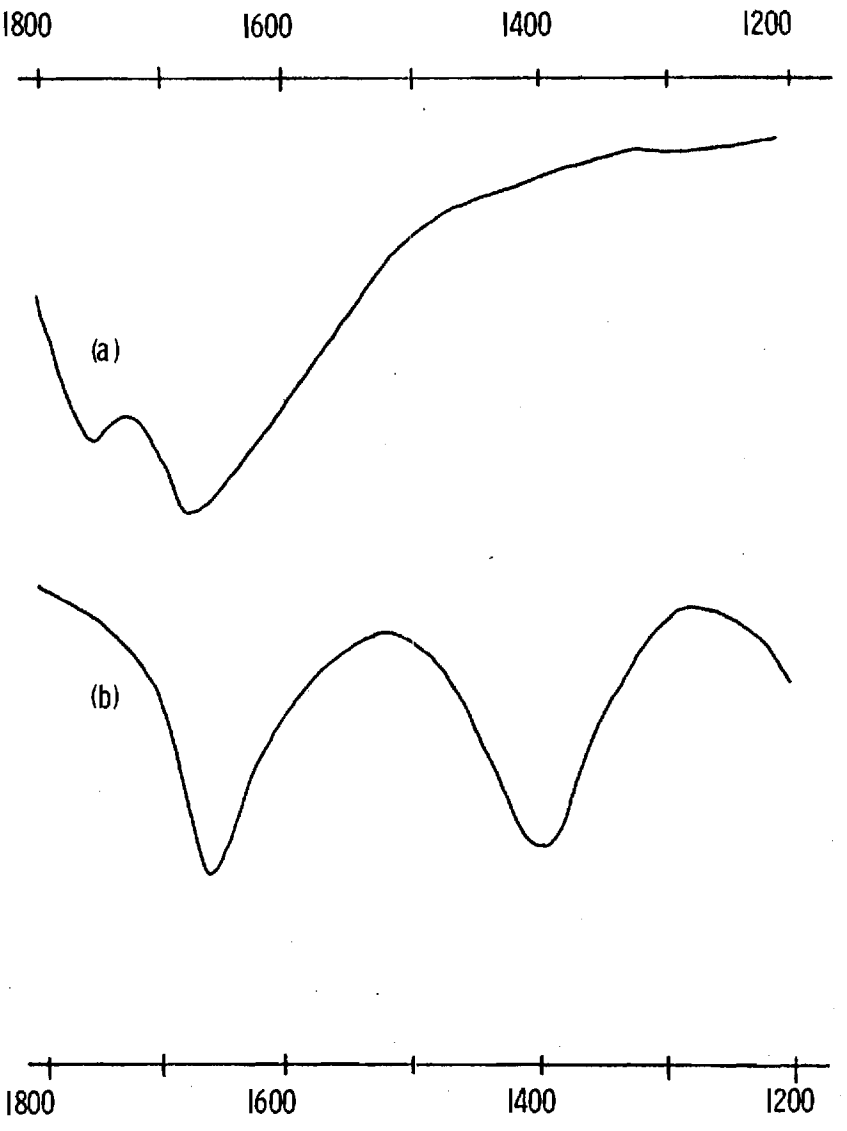
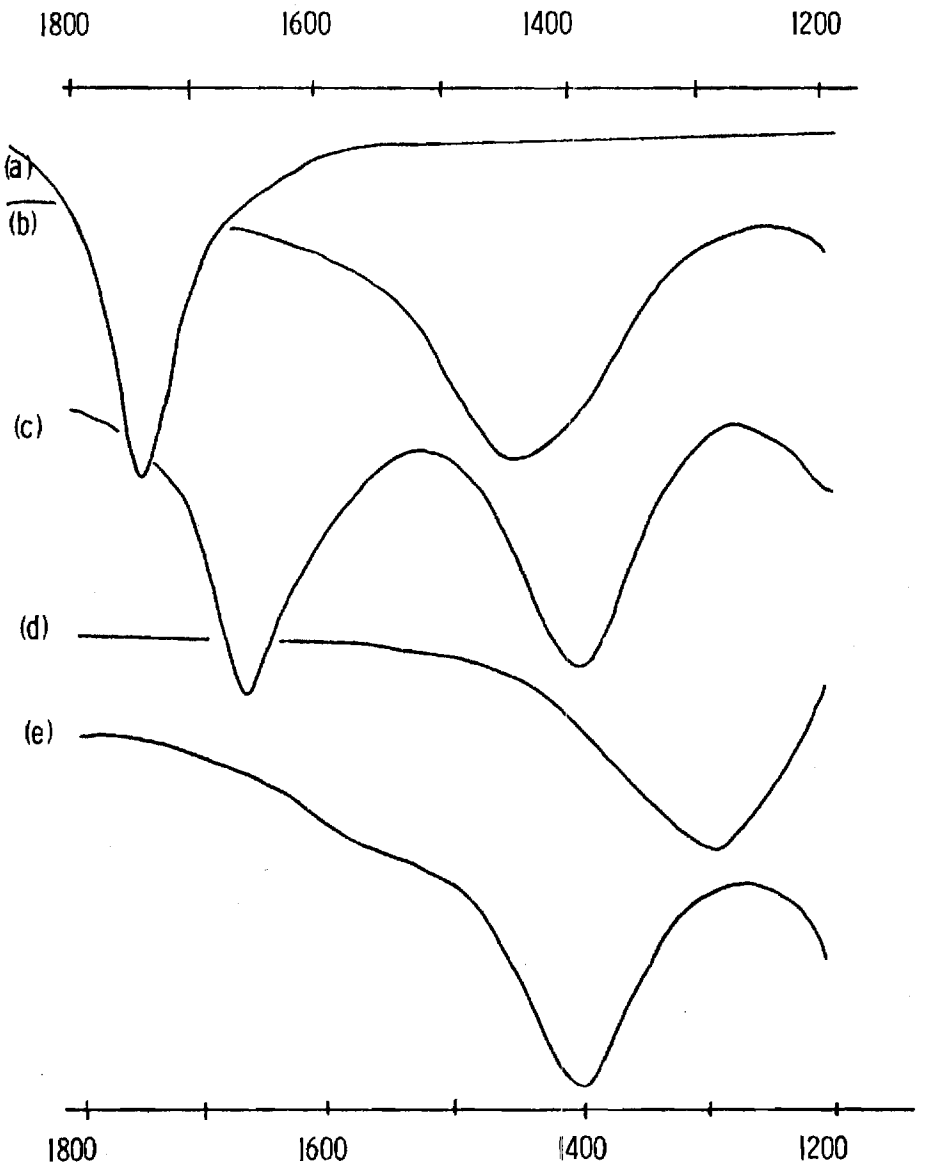

1800
1600
1400
1200
(a)
(b)
1800
1600
1400
1200

Figure 4. 1800-1200 cm^{-1} Region of the Infrared Spectrum for (a) 2:1:1 Mixture of $(CH_3)_2AlH$, $LiAlH_4$, and $LiAl(CH_3)_2H_2$ in THF, (b) $LiZn(CH_3)_2AlH_4$ in THF.


1800
1600
1400
1200
(a)
(b)
(c)
(d)
(e)
1800
1600
1400
1200

Reactions of Alkali Metal Hydrides With Magnesium Alkyls. Preparation of $MMgR_2H$ and MMg_2R_4H Compounds[1,2]

(1) This work was supported by the Office of Naval Research contract No. N00014-67-A-0519-005AD and under ONR Contract Authority No. NR093-050/7-11-69(473)

(2) A preliminary report of this work has appeared; E.C. Ashby and R. Arnott, J. Organometal. Chem., 21, P. 29 (1970).

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ABSTRACT

Lithium hydride was shown not to react with dimethylmagnesium in ether; however in THF intermediate complexes formed which cleaved the THF solvent. Ether cleavage also resulted when LiH and NaH were allowed to react with $(C_6H_5)_2Mg$ in THF. On the other hand, stable insoluble complexes were formed when KH and $(C_6H_5)_2Mg$ were allowed to react in ether solvent. In benzene solvent alkali metal hydrides reacted with R_2Mg compounds to form stable soluble complexes, e.g. $NaMg_2(s\text{-}C_4H_9)_4H$, $KMg(s\text{-}C_4H_9)_2H$ and $KMg(n\text{-}C_4H_9)_2H$. The 1:1 complex of KH and $(s\text{-}C_4H_9)_2Mg$ prepared in benzene is soluble in THF and reacts with LiBr to form $LiMg(s\text{-}C_4H_9)_2H$ and KBr. The corresponding reaction in ether forms the soluble complex, $LiMg_2(s\text{-}C_4H_9)_4H$, and precipitates a mixture of KBr and LiH. The reaction of $KMg(s\text{-}C_4H_9)_2H$ with tri-n-octyl-n-propylammonium bromide in THF produced the $NR_4Mg(s\text{-}C_4H_9)_2H$ compound and the reaction of $KMg(s\text{-}C_4H_9)_2H$ with NaI in THF resulted in the precipitation of KI and the formation of $NaMg(s\text{-}C_4H_9)_2H$.

INTRODUCTION

The reaction of diethylmagnesium with lithium sodium and potassium hydrides is reported to result in complex formation; however, extensive ether cleavage resulted and the complexes could not be isolated.[3] Although stable complexes of beryllium and zinc such as $NaH \cdot Et_2Be$,[4] $NaH \cdot 2Et_2Zn$,[5,6] $LiH \cdot Ph_2Zn$ and $LiH \cdot Ph_2Be$,[7] are known, still no stable complexes of alkali metal hydrides and R_2Mg compounds have been reported.

(3) G.E. Coates and J.A. Heslop, J. Chem. Soc., (A), (1968) 514.

(4) G.E. Coates and G.F. Cox, Chem and Ind., (1962) 269.

(5) P. Kobetz and W.E. Becker, J. Inorg. Chem., 2, (1962) 859.

(6) G.J. Kubas and D.F. Shriver, J. Amer. Chem. Soc., 92, 1949 (1970). ibid. Inorg. Chem., 9, 1951 (1970).

(7) G. Wittig and P. Hornberger, Annalin, 577, (1952) 11.

Our interest in alkali metal complexes of magnesium alkyls resides in the potential of these compounds as intermediates in the preparation of alkali metal complex hydrides of magnesium e.g. $KMgH_3$, $LiMg_2H_5$ etc. Since previous attempts to prepare $LiMgH_3$ by the reaction of LiH and MgH_2 failed,[8] it was felt that either hydrogenolysis or reduction of compounds

(8) J. Tanaka and R. Westgate, Abstracts of Papers, No. 155, 157th ACS National Meeting (1969).

such as $MMgR_2H$ might result in the formation of $MMgH_3$.

$$MMgR_2H \xrightarrow{H_2} MMgH_3 + 2RH \qquad (1)$$
$$MMgR_2H \xrightarrow{LiAlH_4} MMgH_3 + LiAlR_2H_2$$

Since Coates and coworkers[3] had already attempted to prepare $MMgR_2H$ compounds in ether solvents and had observed extensive ether cleavage, it was clear that such complexes would have to be prepared in non ether solvents. Although most R_2Mg compounds are not soluble in hydrocarbon solvents, it has been recently found that $(s\text{-}C_4H_9)_2Mg$ is soluble in benzene.[9] Therefore, it was decided to attempt to carry out these

(9) C.W. Kamienski and J.F. Eastham, J. Org. Chem., 34, 1116 (1969).

reactions in benzene solvent and hence have at least one reactant in solution and also avoid ether cleavage. Reactions between NaH and KH with $(s\text{-}C_4H_9)_2Mg$ in benzene did proceed nicely to form benzene soluble complexes.[2] The reactions were easily monitored by observing the solubilization of the alkali metal hydride as the reaction proceeded.

Experimental Section

Apparatus. All operations were performed under a nitrogen atmosphere using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen and moisture[10] or on the bench top

(10) E.C. Ashby and R. Schwartz, J. Chem. Ed., 51, 65 (1974).

using Schlenk tube techniques.[11] All glassware was flash flamed and

(11) D.F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.

flushed with dry nitrogen prior to use.

Infrared spectra were obtained using a Perkin-Elmer 621 grating spectrophotometer. Cesium iodide windows were used. Solid spectra were recorded as mulls in nujol which had been dried over sodium wire and stored in a nitrogen filled glove box.

X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered CuK_{α} radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hrs. D-spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Hydrogenolysis experiments were performed using a 300 ml Magnedrive autoclave (Autoclave Engineers, Inc.). The chamber was charged either inside the dry box or on the bench top using a hypodermic syringe under strong nitrogen flush. The contents were then heated and stirred under hydrogen for a predetermined period of time. After cooling to room temperature, the chamber was vented and the products were isolated inside the glove box.

Simultaneous DTA-TGA measurements were carried out on a Mettler Thermoanalyzer II. Samples were loaded in alumina or aluminum crucibles using 60 mesh alumina in the reference crucible. Heating rates between 2 and 8°/min were employed. Samples were loaded onto the thermoanalyzer under an atomsphere of argon and during the run a continuous flow of

argon was maintained. Sample weight was monitored at two sensitivities (10 and 1 mg/inch) so that gross weight losses, e.g., solvent, as well as fine losses, e.g., hydrogen could be observed.

Analytical Procedures. Gas analyses were performed by hydrolyzing a measured or weighed sample inside a high vacuum line with ~ 6 M hydrochloric acid and passing the evolved gases through dry ice-acetone and liquid nitrogen traps. Hydrogen was transferred to a calibrated measuring bulb with a Toepler pump. Butane was collected in a separate measured portion of the vacuum line. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum, when present, was masked with triethanolamine. Aluminum determinations were carried out by adding an excess of standard EDTA and then back titrating at pH 4 with standard zinc acetate in water-ethanol with dithizone as indicator. Halide determinations were performed by the Volhard titration. Alkali metals were determined by flame photometry using appropriate filters.

Materials. All solvents were distilled immediately prior to use. Tetrahydrofuran and benzene (Fisher Certified reagent grade) were distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher reagent) over $LiAlH_4$. Benzyl chloride (Fisher reagent grade) was distilled over P_2O_5 under reduced pressure and 2-chloropropane and 1-chloropentane (Eastman Organic Chemicals) were dried and distilled over $MgSO_4$ prior to use. Grignard grade magnesium turnings were used except in the preparation of dimethylmagnesium where triply sublimed magnesium (Dow Chemical Company) was employed. Secondary-butyllithium was obtained as a 11.9% solution in hexane from the Foote Mineral Company and stored at -20° until ready to use. Methyllithium used was a 5.0% solution in diethyl ether obtained from the Lithium Corporation of America. Lithium bromide and lithium iodide (Foote Mineral Company) were dried at 130° under

vacuum for 24 hr and used without further purification. Tri-n-octyl-n-propyl ammonium bromide (Eastman Organic Chemicals) was dried at 55° under vacuum for 2 days and used without any subsequent purification. Ultrapure hydrogen (99.9995%) obtained from Matheson Corporation was employed in hydrogenation experiments. Dimethylmercury was obtained from Orgmet, Inc., and used without further purification. Potassium and sodium hydride (as a suspension in mineral oil), $LiAlH_4$ and $NaAlH_4$ were obtained from Ventron Metal Hydrides Division. Solutions of $LiAlH_4$ and $NaAlH_4$ in diethyl ether or tetrahydrofuran were prepared by making a slurry of the compounds in the respective solvents, stirring for 48 hr, followed by centrifugation and filtration. All solutions were freshly analyzed immediately before use. Other materials such as $(CH_3)_2Mg$[12] and $(s\text{-}C_4H_9)_2Mg$[9]

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(12) E.C. Ashby and R. Arnott, J. Organometal. Chem., 14, 1 (1968).

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were prepared according to methods described previously. Active NaH was prepared by hydrogenation of 0.5 mole of sodium in 150 ml of benzene at 400°F and 3,000 psi H_2 in a 300 ml magne-stirrer autoclave. The Na:H ratio was 1.0:1.0. Active potassium hydride was prepared similarly except that the reaction temperature was 300°F. Active LiH was prepared by reaction of t-butyllithium (150 ml of 1.25 molar solution) in pentane with hydrogen at 3,000 psi at room temperature for 16 hours. Li:H ratio of the resulting slurry was 1.0:1.0.

Reactions of Alkali Metal Hydrides with Magnesium Alkyls and Aryls. Attempted Preparation of $LiMg(CH_3)_2H$ in Ether. Dimethylmagnesium (51.12 ml of a 0.66 molar solution, 33.6 mmoles) was added to LiH

(0.267 g, 33.6 mmoles) and the mixture stirred for 24 hours. Analysis of an aliquot of the supernatent indicated that no reaction had taken place. The mixture was then refluxed for an additional 40 hours and after cooling taken into the dry box and filtered. Analysis of the filtrate revealed that all of the magnesium was still in solution, and that no lithium was present. The IR spectrum of the filtrate was identical to that of $(CH_3)_2Mg$ in ether. The residue was shown by analysis to be LiH. Anal. Calcd for LiH: Li, 87.4%; H, 12.6%. Found: Li, 87.0%; H, 12.6%.

Attempted Preparation of $LiMg(CH_3)_2H$ in THF. Dimethylmagnesium (20.0 ml of a 0.93 molar solution, 18.6 mmoles) was added to LiH (0.6629 g, 83.5 mmoles) and the mixture stirred at reflux for 36 hours and then filtered. The filtrate was found to contain 18 mmoles of magnesium and 1.2 mmoles of lithium (Li:Mg ratio, 1:15). Analysis revealed that the residue was mainly lithium hydride. Anal. Calcd for LiH: Li, 87.4%; H, 12.6%. Found: Li, 81.2%. A trace of magnesium was found in the residue.

In a similar experiment a mixture of dimethylmagnesium and lithium hydride was stirred at 25° for 7 days and then filtered. The filtrate again revealed a Li:Mg ratio of 1:15. Gas evolution indicated 20% loss of the methyl groups.

Attempted Preparation of $LiMg(C_6H_5)_2H$ in THF. Diphenylmagnesium (35.0 ml of a 0.915 molar solution, 32 mmoles) was added to LiH (0.646 g, 81 mmoles) in a 200 ml round bottom flask containing 35 ml of THF. The sample was refluxed for several days, allowed to cool, and filtered in the dry box. Analysis of the filtrate revealed a Li:Mg ratio of 0.61:

1.00, with 80% of the magnesium recovered in the filtrate. No hydrogen was evolved on hydrolysis of the filtrate.

Attempted Preparation of $NaMg(C_6H_5)_2H$ in Ether. Diphenylmagnesium (71 ml of a 0.52 molar solution, 36.8 mmoles) was stirred with NaH (0.883 g, 36.8 mmoles) for 5 days at 25°. The reaction mixture was then filtered in the dry box. Analysis of the filtrate revealed a Li:Mg ratio of 0.38:1.00 with 83% of the magnesium recovered in the filtrate. No hydrogen was evolved on hydrolysis of the filtrate.

Preparation of $KMg(C_6H_5)_2H \cdot Mg(C_6H_5)_2$ in Ether. Potassium hydride and $(C_6H_5)_2Mg$ were mixed in diethyl ether in several stoichiometries to give K:Mg ratios from 0.33:1 to 5:1. In all cases an insoluble complex formed.

In a typical reaction $(C_6H_5)_2Mg$ (50 ml of a 0.8 molar solution in diethyl ether, 40 mmoles) was added to KH (3.20 g, 80 mmoles) in 50 ml of ether. The mixture was stirred for 3 days and filtered. Analysis of the filtrate revealed that all of the magnesium containing species had precipitated.

In a similar reaction where the initial K:Mg ratio was 1:3, only 66% of the magnesium containing species precipitated, leaving the remainder of the $(C_6H_5)_2Mg$ in solution. In this case a 1:2 complex $KH \cdot 2Mg(C_6H_5)_2$ was formed. The solid residues were analyzed and gave the following results. (Benzene was determined by difference.) Anal. Calcd for $KH \cdot 2Mg(C_6H_5)_2$: K, 9.85%; Mg, 12.25%; C_6H_6, 77.65%; H, 0.25. Found: K, 10.52%; Mg, 11.0%; C_6H_6, 78.3%; H, 0.25%. When 2 equivalents of $(C_6H_5)_2Mg$ was allowed to react with one equivalent of KH, analysis indicated a K:Mg:H ratio of 1.18:2.00:1.26. The X-ray diffraction pattern indicated

occluded KH. If this is subtracted from the analysis, the ratio is 1.00: 2.00:1.08. (Found: K, 9.90%; Mg, 11.3%; C_6H_6, 78.54%; H, 0.25%.) Calcd for $KH \cdot Mg(C_6H_5)_2$: K, 17.94%; Mg, 11.10%; C_6H_6, 70.50%; H, 0.46%. Found: K, 16.35%; Mg, 10.20%; C_6H_6, 73.09%; H, 0.36%. Calcd for $2KH \cdot Mg(C_6H_5)_2$: K, 30.40%; Mg, 9.40%; C_6H_6, 59.40%; H, 0.80%. Found: K, 29.20%; Mg, 9.40%; C_6H_6, 60.60%; H, 0.72%. Calcd for $5KH \cdot Mg(C_6H_5)_2$: K, 51.60%; Mg, 6.42%; C_6H_6, 40.76%; H, 1.32%. Found: K, 54.70%; Mg, 6.56%; C_6H_6, 38.49%; H, 1.25%. The X-ray powder pattern for each of these solids is reported in Table 1.

Attempted Preparation of $NaMg(n\text{-}C_7H_{15})_2H$ in Hexane. Di-n-heptylmagnesium (77.8 ml of a 0.093 molar solution, 7.2 mmoles) and sodium hydride (0.173 g, 7.2 mmoles) were stirred for 18 hours at reflux temperature. Filtration produced a clear colorless solution and a gray solid. Analysis revealed that the filtrate contained 7.0 mmoles (95%) of the magnesium species and no sodium. The residue was shown by analysis to be sodium hydride. Anal. Calcd for NaH: Na, 95.8%; H, 4.2%. Found: Na, 94.5%; H, 3.9%. Under similar conditions KH also failed to react with $(n\text{-}C_7H_5)_2Mg$ after 72 hours at reflux temperature in hexane solvent.

Attempted Preparation of $LiMg(s\text{-}C_4H_9)_2H$ in Benzene. A mixture of $Mg(s\text{-}C_4H_9)_2$ (30.0 ml of a 0.58 molar solution, 17.4 mmoles) and active LiH (prepared from $t\text{-}C_4H_9Li$ and H_2) (5 ml of a pentane slurry, 9.5 mmoles) was stirred at room temperature for three days. Analysis of a portion of the supernatent liquid indicated that no reaction had occurred. All of the magnesium was still in solution and no LiH had dissolved. The reaction mixture was then heated to 40° for an additional two days.

Analysis again revealed that no reaction had taken place.

Preparation of $NaMg_2(s\text{-}C_4H_9)_4H$ in Benzene. Di-s-butylmagnesium (101 ml of a 0.496 molar solution, in benzene, 50 mmoles) was added to NaH (0.6559 g, 27.4 mmoles) and stirred for two days. Analysis of the resulting solution showed a Na:Mg:C_4H_9:H ratio of 0.90:2.0:3.96:0.85. The nmr spectrum and the IR spectrum of the solution were significantly different from that of $Mg(s\text{-}C_4H_9)_2$.

In a similar experiment, one equivalent of NaH and $Mg(s\text{-}C_4H_9)_2$ were combined under the above conditions. Once the ratio of Na:Mg in solution reached 0.45:1.0, no further uptake of sodium was observed even after several days.

Preparation of $KMg(s\text{-}C_4H_9)_2H$ in Benzene. Potassium hydride (1.138 g, 28.4 mmoles) was slurried with 50 ml of freshly distilled benzene and added to $(s\text{-}C_4H_9)_2Mg$ (95 ml of a 0.30 molar solution, 28.4 mmoles) with rapid stirring. After twenty hours the mixture was filtered producing a strawcolored filtrate and a darker residue ($\sim$ 100 mg). Analysis of an aliquot of the solution showed a K:Mg:C_4H_9:H ratio of 1.0:1.0:1.9:0.95. The yield was $>$ 90%. Cryoscopic molecular weight measurements indicated a monomer-dimer equilibrium over a concentration range 0.06 - 0.16 molal.

Successful synthesis was also carried out in benzene-cyclohexane mixtures. The complex $KMg(s\text{-}C_4H_9)_2H$ was insoluble in pure alkanes, however, and attempted synthesis in cyclohexane alone proved unsatisfactory.

Preparation of $KMg(n\text{-}C_4H_9)_2H$ in Benzene. Potassium hydride (28.8 mmoles) in 190 ml of freshly distilled benzene was added to $(n\text{-}C_4H_9)_2Mg$ (31.0 mmoles) and stirred at 40° for 48 hours. Analysis of an aliquot of the filtrate revealed a K:Mg ratio of 0.97:1.0. The filtrate was 0.11 molar in complex (70% yield). Cryoscopic molecular weight measurements indicated a dimeric species in benzene over a concentration range 0.08 - 0.32 molal (Fig. 2).

Attempted Preparation of $K_2Mg(s\text{-}C_4H_9)_2H_2$ in Benzene. Potassium hydride (1.193 g, 29.8 mmoles) slurried with 50 ml of benzene was added to $KMg(s\text{-}C_4H_9)_2H$ (99.5 ml of a 0.306 molar solution, 30.4 mmoles). The mixture was stirred for 18 hours and then filtered. A light straw-colored solution and a tan solid were separated. Analysis of the filtrate revealed that nearly quantitative precipitation of the magnesium containing species had occurred. Analysis of the solid gave the following results. Anal: Calcd for $K_2Mg(s\text{-}C_4H_9)_2H_2$: Mg, 11.10%; Bu, 52.20%; H, 0.95%. Mg:Bu:H = 1.0:2.0:2.0. Found: Mg, 10.2%; Bu, 16.20% H, 0.89%. Mg:Bu:H = 1.0:0.67:2.1.

The IR spectrum of this solid showed the strong C-Mg stretching band at 521 cm^{-1}, attributable to butyl-magnesium stretching, was severely diminished in the supposed 2:1 complex. In addition, when the solid was added to a dry-ice ether slurry under nitrogen and the resulting mixture acidified, appreciable quantities of benzoic acid and methyl-butyric acid was produced. Similar results were obtained when two equivalents of KH were allowed to react with one equivalent of $(s\text{-}C_4H_9)_2Mg$ under similar reaction conditions.

Metal Exchange Reactions.

Preparation of $LiMg_2(s\text{-}C_4H_9)_4H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$ with Lithium Bromide in Ether. $KMg(s\text{-}C_4H_9)_2H$ was prepared by the reaction of potassium hydride with $(s\text{-}C_4H_9)_2Mg$ in benzene. The benzene was removed under vacuum resulting in an orange-red viscous residue. This was dissolved in diethyl ether to give a clear solution and used immediately. 2.763 g of lithium bromide (31.8 mmoles) was dissolved in 100 ml ether and added to 141.3 ml of the $KMg(s\text{-}C_4H_9)_2H$ solution in ether (0.225 M in K^+; 31.8 mmoles) with vigorous stirring. The mixture was stirred for 6 hr and then filtered. The white precipitate was washed several times with ether and dried under vacuum at room temperature for 4 hr. The light orange filtrate on analysis gave the following ratios: $Li:Mg:C_4H_9:H = 0.56:1.00:2.0:0.50$. Potassium and bromine were absent. The precipitate gave the following ratios: $Li:K:H:Br = 1.0:2.0:1.0:1.9$.

Preparation of $LiMg(s\text{-}C_4H_9)H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$ with LiBr in THF. To lithium bromide (8.52 g, 98.1 mmoles) dissolved in 100 ml of THF was added 255.7 ml of 0.384 M solution of $KMg(s\text{-}C_4H_9)_2H$ in THF. A precipitate formed immediately was shown to be KBr. The filtrate, on solvent removal under vacuum, produced a viscous, orange material. Analysis produced the following $Li:Mg:C_4H_9:H$ ratio: 1.00:1.12:2.04:0.93. Potassium and bromide analyses were negative.

Preparation of $NaMg(s\text{-}C_4H_9)_2H$. Reaction of Sodium Iodide with $KMg(s\text{-}C_4H_9)_2H$ in THF. 105 ml of a sodium iodide solution in THF (0.252 M; 26.5 mmoles) was added, with stirring, to 125 ml of a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in THF (25.2 mmoles in Mg). An immediate creamy yellow precipitate formed. After stirring for 4 hr,

the mixture was filtered and the precipitate washed with several small portions of THF. The precipitate was found to be potassium iodide upon analysis. The filtrate exhibited a composition corresponding to $NaMg(s\text{-}C_4H_9)_2H$.

Preparation of $R_4NMg(s\text{-}C_4H_9)_2H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$ with R_4NBr in THF. To tri-n-octyl-n-propylammonium bromide (5.32 g, 11.17 mmoles) in 25 ml THF was added 50 ml of 0.222 M THF solution of $KMg(s\text{-}C_4H_9)_2H$. After 30 min a precipitate began to form. After overnight stirring the mixture was filtered. Analysis of the light orange filtrate gave a $Mg:C_4H_9:H$ ratio of 1.00:1.90:0.92. Potassium and bromine were absent. The precipitate was shown to be KBr. On complete solvent removal, a light orange oily product resulted.

Results and Discussion

Formation of $MM'R_2H$ and $MM'_2R + H$ Compounds

Reactions of LiH, NaH and KH with $(CH_3)_2Mg$, $(C_2H_5)_2Mg$ and $(C_6H_5)_2Mg$.

When lithium hydride was allowed to reflux with dimethylmagnesium in diethyl ether no reaction was observed; however, when THF was used as the solvent some reaction took place over a 36 hour reflux period. After filtering the reaction mixture, analysis of the resulting solution indicated a Li:Mg ratio of 1:15. The residue was shown by analysis to consist mainly of unreacted lithium hydride. In a similar experiment, LiH and $(CH_3)_2Mg$ were stirred for 7 days at 25°. Analysis of the reaction filtrate again revealed a Li:Mg ratio of 1:15. The amount of gas evolved on hydrolysis indicated that the number of methyl groups in solution had decreased by 20%. Similar results were noted by Coates[3] when higher temperatures and shorter reaction times were employed.

Several experiments were conducted using $(C_6H_5)_2Mg$. When a mixture of LiH and $(C_6H_5)_2Mg$ was allowed to reflux for several days in THF, analysis of the filtrate revealed a Li:Mg ratio of 0.61:1.00. No hydrogen was evolved on hydrolysis of the solution indicating that ether cleavage had occurred. Similar results were obtained by mixing sodium hydride with $(C_6H_5)_2Mg$ in diethyl ether. After 5 days at 25° the reaction mixture was filtered and analysis of the filtrate revealed a Na:Mg ratio of 0.38:1.00. Again, no hydride was evolved on hydrolysis of the solution.

In contrast, the reaction of KH with $(C_6H_5)_2Mg$ in ether, at K:Mg ratios ranging from 0.3:1 to 5:1 resulted in complex formation. Precipitation of the complex must have occurred faster than ether cleavage could take place. When KH and $(C_6H_5)_2Mg$ were mixed in 1:3 molar ratio, 66% of the

magnesium containing compound precipitated from solution. Since only 2/3 of the magnesium species precipitated, the limiting ratio of K:Mg in the complex must therefore be 1:2.

$$KH + 2(C_6H_5)_2Mg \longrightarrow KMg(C_6H_5)_2H \cdot Mg(C_6H_5)_2 \qquad (2)$$

This particular stoichiometry has been observed several other times in complexes of this type.[4, 13] When the K:Mg molar ratio was increased

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(13) P. Kobetz and W.E. Becker, J. Inorg. Chem., 2, 859 (1962).

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stepwise to 5:1, quantitative precipitation of the magnesium containing species occurred.

The X-ray powder patterns were recorded for each of the above solids and the d spacings are given in Table 1. Lines assigned to potassium hydride at d spacings of 3.81, 3.27, 2.84, 2.61, 2.02 and 1.71 Å were observed in 1:1, 2:1 and 5:1 mixtures. The strongest line for potassium hydride at 3.24 Å was very faint in the 0.5:1 compound. Lines at d spacings of less than 2.26 Å were too weak to be read accurately. Lines attributed to complex formation decreased in intensity as this species was diluted with solid potassium hydride. It appears that the 1:2 complex, $KMg(C_6H_5)_2H \cdot Mg(C_6H_5)_2$ is the only stable complex formed between KH and $(C_6H_5)_2Mg$.

Reaction of KH With $(s\text{-}C_4H_9)_2Mg$ in Benzene.

Of considerably more interest is the formation of stable complexes

in solvents in which ether cleavage is avoided. In this connection the hydrocarbon soluble $(s\text{-}C_4H_9)_2Mg$ recently reported by Kamienski and Eastham[9] is an excellent candidate for the preparation of stable complexes of dialkylmagnesium compounds with alkali metal hydrides.

When di-s-butylmagnesium was stirred with an equivalent amount of potassium hydride in either benzene or a 50:50 benzene-cyclohexane mixture, the hydride species dissolved and a stable soluble 1:1 complex formed.

$$KH + (s\text{-}C_4H_9)_2Mg \longrightarrow KMg(s\text{-}C_4H_9)_2H \qquad (3)$$

An attempt to prepare the complex in pure cyclohexane was unsuccessful, largely due to the fact that potassium di-s-butylhydridomagnesium is insoluble in this solvent and only an oily gummy residue resulted. When commercial potassium hydride was employed, the reaction mixture was stirred overnight in order to achieve a yield on the order of 90%, but when "active" potassium hydride (freshly prepared) was employed, the reaction was complete in less than one hour. The nmr spectrum of the 1:1 complex is shown in Figure I. The signal observed at 3.40 δ is attributed to the hydridic hydrogen in the complex. Integration of the α-hydrogen of the secondary butyl group and the hydridic hydrogen gave a ratio of 1.00:0.83 consistent with complex formation. The position of the hydride signal was similar to that observed by Shriver[6] for $NaH \cdot 2Et_2Zn$. An ether solution of the 1:1 complex was shown by nmr to be stable for at least 1 hour at room temperature. The ether cleavage then observed for the 1:1 complex in ether solvent was therefore a

consequence of both higher temperature and longer reaction time. Comparison of the infrared spectra of $(s\text{-}C_4H_9)_2Mg$ and $KMg(s\text{-}C_4H_9)_2H$ were not nearly as informative as the nmr comparison. Cryoscopic molecular weight measurements in benzene indicated a monomer-dimer equilibrium over a concentration range 0.06 - 0.16 molal. These data are shown in Figure 2.

Reaction of KH With $(n\text{-}C_4H_9)_2Mg$ in Benzene.

A second complex was prepared analogous to that described above in which the R group was n-butyl instead of s-butyl. Initially, potassium hydride was stirred with an equivalent amount of $(n\text{-}C_4H_9)_2Mg$ in benzene at 40°. After 48 hours analysis of an aliquot of the supernatent revealed a K:Mg ratio of 0.97:1.0 and the concentration of magnesium was shown to be 0.11 mmoles/ml. As was observed in the previous example, a soluble complex was not formed in cyclohexane.

$$KH + (n\text{-}C_4H_9)_2Mg \longrightarrow KMg(s\text{-}C_4H_9)_2H \qquad (4)$$

The nmr spectrum of a 0.378 molar solution of $KMg(n\text{-}C_4H_9)_2H$ in benzene at 25° was consistent with complex formation. The triplet attributed to the α methylene protons was observed at -0.59 δ and a low intensity signal was observed at 3.47δ which was attributed to the hydridic hydrogen. Cryoscopic molecular weight measurements (figure 2) indicate that $KMg(n\text{-}C_4H_9)_2H$ is dimeric over a concentration range 0.08 - 0.32 molal in benzene.

Reaction of NaH With $(s\text{-}C_4H_9)_2Mg$ in Benzene.

When sodium hydride and $(s\text{-}C_4H_9)_2Mg$ were stirred in benzene, a

complex was formed in which the Na:Mg ratio was 1:2.

$$NaH + 2(s\text{-}C_4H_9)_2Mg \longrightarrow NaMg(s\text{-}C_4H_9)_2H\cdot(s\text{-}C_4H_9)_2Mg \qquad (5)$$

The same results were observed even when the reagents were mixed in a molar ratio of 1:1 and the reaction mixture was stirred for several days.

The nmr spectrum of a 0.23 molar solution of the complex in benzene was recorded at room temperature using benzene as the internal standard. The spectrum was similar to that observed for $KMg(s\text{-}C_4H_9)_2H$ with hydridic hydrogen observed at 3.40 δ.

Reaction of LiH With $(s\text{-}C_4H_9)_2Mg$ in Benzene.

Several attempts to prepare a complex by mixing lithium hydride and $(s\text{-}C_4H_9)_2Mg$ in benzene were unsuccessful. Even when extremely reactive lithium hydride, prepared by low temperature hydrogenation of t-butyllithium in pentane, was used; no reaction was observed after several days. The nmr spectrum of the filtrate obtained form this reaction mixture was identical to that of $(s\text{-}C_4H_9)_2Mg$ in benzene. Analysis revealed that none of the lithium hydride had dissolved and all of the magnesium remained in solution.

Reaction of Excess KH With $(s\text{-}C_4H_9)_2Mg$ in Benzene.

Repeated attempts were made to prepare an authentic 2:1 complex by mixing potassium hydride with $(s\text{-}C_4H_9)_2Mg$ in benzene in a 2:1 molar ratio. Invariably, all of the magnesium containing species precipitated and could be isolated by filtration of the reaction mixture. Analysis of this residue indicated that extensive metallation of the solvent had occurred. When a portion of the solid was carboxylated both 2-methylbutyric acid

and benzoic acid were produced. The X-ray powder diffraction pattern revealed that some potassium hydride had been occluded in the solid. Similar results were obtained when a previously prepared solution of potassium di-s-butylhydridomagnesium was added to a benzene slurry of potassium hydride. All of the magnesium containing species again precipitated and the residue was found to be identical to the solid described above.

The results of these experiments were quite interesting. It had been observed earlier that when a benzene solution of $KMg(s\text{-}C_4H_9)_2H$ was allowed to stand at room temperature, a precipitate containing phenyl groups bonded to magnesium was formed slowly, whereas $KMg(n\text{-}C_4H_9)_2H$ was stable under these conditions. Furthermore, if a slight excess of KH was used in the preparation of the s-butyl complex, the yield of 1:1 complex was significantly decreased. Apparently complexation with a second equivalent of potassium hydride greatly enhanced the ionic character of the C-Mg bond and metallation of the solvent occurred fairly rapidly. Since both the nmr spectra of earlier preparations of the 1:1 complex and elemental analysis indicated a good K:Mg:Bu:H ratio in solution even when a slight excess of potassium hydride was used, it was concluded that as metallation occurs to form a new species in which the magnesium is bonded to a phenyl group, precipitation of this species is immediate.

$$\begin{matrix} 2KH + (s\text{-}C_4H_9)_2Mg \\ KH + KMg(s\text{-}C_4H_9)_2Mg \end{matrix} \longrightarrow K_2Mg(s\text{-}C_4H_9)_2H_2 \xrightarrow{C_6H_6} K_2Mg(s\text{-}C_4H_9)(C_6H_5)H_2 \qquad (6)$$

$$K_2Mg(s\text{-}C_4H_9)(C_6H_5)H_2 \xrightarrow{CO_2} \xrightarrow{H^+} CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{C}}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH + C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH \qquad (7)$$

Similar examples of enhanced reactivity of an alkyl group bonded to a metal atom upon complexation have been reported in the literature. Rausch and Ciappenelli[14] reported that n-butyllithium-N,N,N',N',-

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(14) M.D. Rausch and D.J. Ciappenelli, J. Organometal. Chem., 10, 127 (1967).

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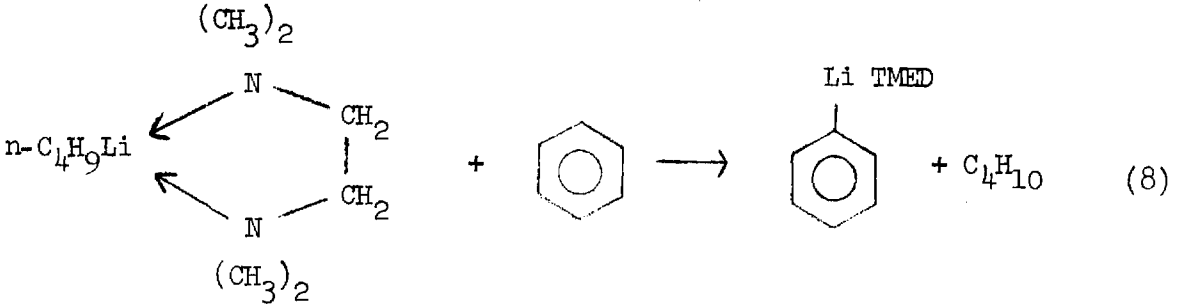
tetramethylethylenediamine metallated benzene and ferrocene. Similarly,



(8)

Langer[15] reported that this same complex metallated benzene and produced

(15) A.W. Langer, Trans. N. Y. Acad. Sci., 27, 745 (1965).

phenyllithium. Since butyllithium itself is unreactive toward benzene, the increased reactivity of the lithium reagent was attributed to complexation with an electron donating basic species.

Potassium Exchange in Reactions With $KMg(s\text{-}C_4H_9)_2H$.

Although the direct reaction of KH with $(s\text{-}C_4H_9)_2Mg$ did not proceed in tetrahydrofuran, the compound $KMg(s\text{-}C_4H_9)_2H$ prepared from benzene dissolved readily in THF. The solution was not very stable at room temperature; however, at low temperature it was found to be stable up to five days, and no THF cleavage was observed.

When a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ was added to tri-n-octyl-n-propyl ammonium bromide in THF, quantitative precipitation

$$KMg(s\text{-}C_4H_9)_2H + N(C_8H_{17})_3(C_3H_7)Br \longrightarrow N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H + KBr \qquad (9)$$

of KBr took place and the filtrate upon solvent removal produced the oily orange $N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H$. Analysis of the THF solution of this compound was not quite as difficult as the product prepared in benzene solution. The Mg:Butyl:H ratios were found to be 1:1.90:0.92.

The infrared spectrum of the neat material was similar to that of $KMg(s\text{-}C_4H_9)_2H$ with the characteristic broad absorption envelope between 1200 and 600 cm^{-1} (ν Mg-H).

When a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in tetrahydrofuran was added to an equivalent amount of lithium bromide in THF, KBr precipitated quantitatively during overnight stirring.

$$KMg(s\text{-}C_4H_9)_2H + LiBr \xrightarrow{THF,\ 25^\circ} LiMg(s\text{-}C_4H_9)_2H + KBr \qquad (10)$$

Analysis of the clear filtrate gave the following ratios: Li:Mg: Butyl:H = 1.00:1.12:2.04:0.93. Upon solvent removal under vacuum, an orange viscous material resulted. It was very difficult to remove the last traces of solvent at room temperature, even under high vacuum. The viscous product readily dissolved in benzene giving a clear orange solution. NMR spectra of this benzene solution showed the presence of a small amount of tetrahydrofuran. The infrared spectrum of this product was identical with the analogous potassium and tetra-alkylammonium compounds. Tetrahydrofuran solutions of $LiMg(s\text{-}C_4H_9)_2H$ at room temperature are apparently more stable than that of the potassium compound. When a benzene solution of $KMg(s\text{-}C_4H_9)_2H$ was added to a lithium bromide slurry in benzene, no reaction occurred even after several days of stirring. No lithium was detected in the supernantant solution which essentially retained its original composition.

There is an interesting basic difference between the reactions of $KMg(s\text{-}C_4H_9)_2H$ with lithium bromide in THF and diethyl ether. In the

case of tetrahydrofuran, $LiMg(s\text{-}C_4H_9)_2H$ is formed; however, when diethyl ether is the solvent, $LiMg_2(s\text{-}C_4H_9)_4H$ is the product.

$$2KMg(s\text{-}C_4H_9)_2H + 2LiBr \xrightarrow[25°]{Et_2O} LiMg_2(s\text{-}C_4H_9)_4H + 2KBr + LiH \qquad (11)$$

The solid product obtained from this reaction was analyzed and found to be a mixture of KBr and LiH formed in 2:1 ratio. It seems reasonable to suggest that $LiMg(s\text{-}C_4H_9)_2H$ is formed in the reaction and that it slowly disproportionates to $LiMg_2(s\text{-}C_4H_9)_4H$ and LiH .

On addition of sodium iodide to $KMg(s\text{-}C_4H_9)_2H$ in THF, a quantitative precipitate of KI was obtained. Analysis of the resulting solution

$$KMg(s\text{-}C_4H_9)_2H + NaI \xrightarrow[25°]{THF} NaMg(s\text{-}C_4H_9)_2H + KI \qquad (12)$$

showed a Na:Mg:Bu:H ratio of 1.00:1.07:1.87:0.92 establishing the formation of $NaMg(s\text{-}C_4H_9)_2H$ in solution.

Figure 1. NMR Spectrum of Potassium Di-s-butylhydridomagnesium in Benzene.

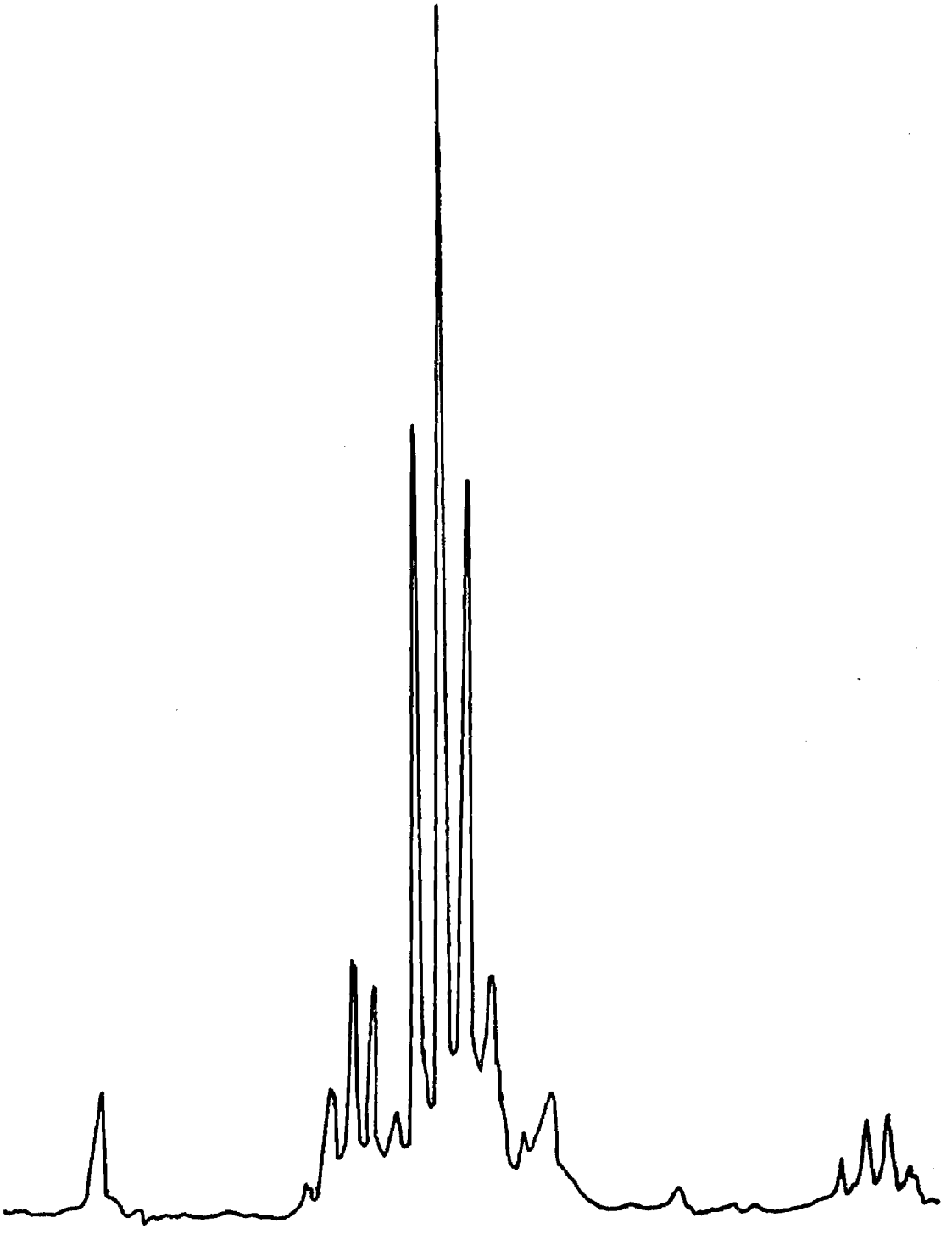


Figure 2. Association of Potassium Di-s-butylhydridomagnesium -o-, and Potassium Di-n-butylhydridomagnesium in Benzene.

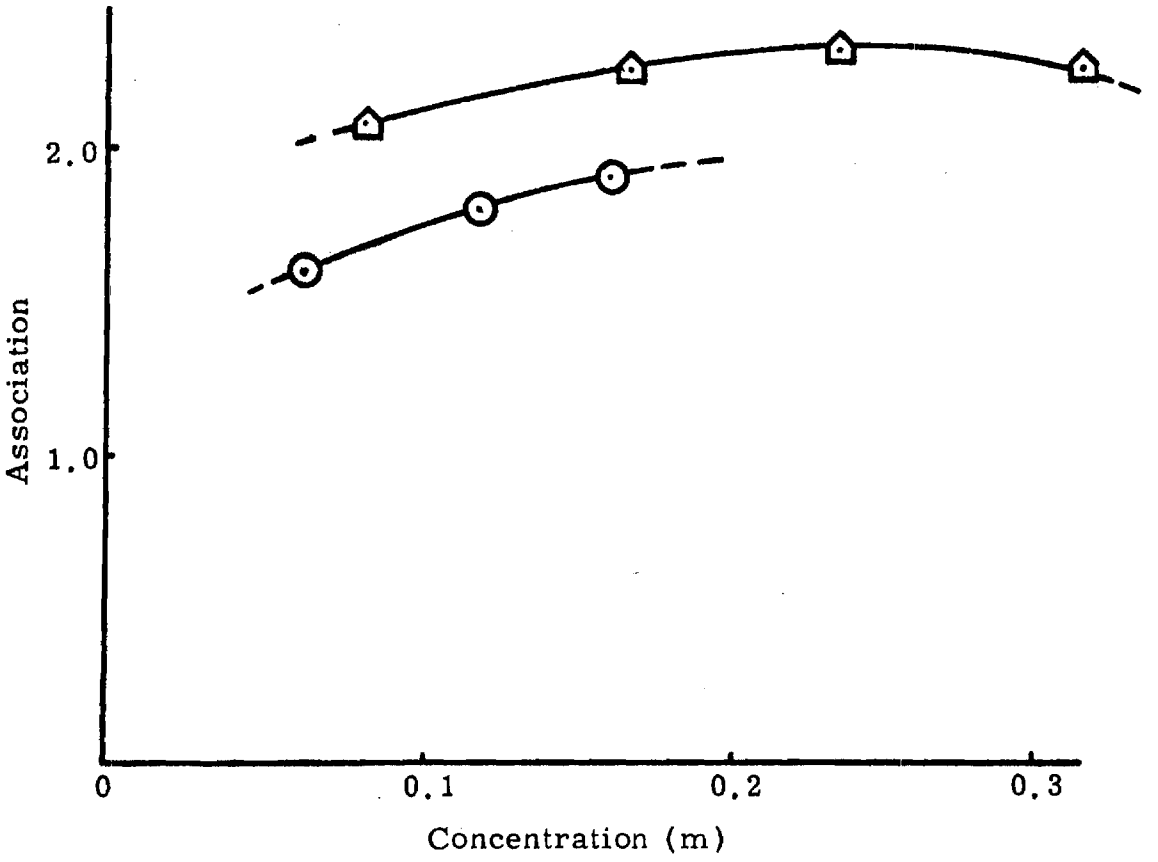

Association
2.0
1.0
0
0.1
0.2
0.3
Concentration (m)

Table 1

X-Ray Powder Diffraction Pattern of Potassium Hydride-Diphenylmagnesium Complexes

$KH + 2Mg(C_6H_5)_2$		$KH + Mg(C_6H_5)_2$		$2KH + Mg(C_6H_5)_2$		$5KH + Mg(C_6H_5)_2$	
d	I	d	I	d	I	d	I
		8.74	w	8.68	w-br		
8.00	w	8.00	vvw				
7.42	w	7.46	vvw	7.36	vvw		
6.50	w	6.50	vvw	6.47	vvw		
5.80	w	5.88	vvw	5.85	vvw		
5.10	m	5.15	w	5.12	w-br	5.19	vvw
4.76	w	4.71	vw	4.82	vw		
4.50	w	4.37	w-br	4.39	w-br	4.44	vvw
4.35	m	4.19	vw	4.19	vw		
4.16	w	4.05	vw	4.04	vw		
4.00	w	3.81	vvw	3.82	vvw		
3.75	w	3.75	vvw	3.63	vvw	3.64	vvw
3.45	w	3.27	m	3.28	vs	3.28	vs
3.25	vw	3.06	vw	3.05	vw	3.19	vvw
3.04	m	2.93	vvw	2.93	m	2.84	s
2.92	m	2.84	m	2.85	m		
2.81	m	2.70	vw	2.69	vvw		
2.67	vw	2.61	vvw	2.61	vvw	2.60	vvw
2.59	vw	2.29	vvw	2.50	w-br	2.23	vvw
2.48	w-br	2.02	w	2.02	m		
2.32	w	1.72	w	1.91	vvw	1.91	vvw
2.26	w			1.72	m	1.71	m

Reactions of Aluminum Hydride with Groups I and II A and B Metal Halides

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Abstract

The reaction of aluminum hydride with several group II A and B metal halides in diethyl ether has been studied in detail. Hydrogen-halogen exchange in the system AlH_3-MX_2 (where M = Ca, Mg, Zn, Cd and Cu and X = Cl, Br, and I) has been found to depend on the electronegativities of the metals concerned. Thus, calcium bromide and magnesium bromide did not undergo exchange with aluminum hydride whereas zinc chloride and zinc bromide did react with aluminum hydride to produce a new complex metal hydride of the type H_3Zn_2X (where X = Cl, or Br). The reaction of zinc iodide with aluminum hydride yielded a complex of the composition $ZnI_2 \cdot AlH_3$. Cadmium bromide reacted very slowly with aluminum hydride at -40° to yield a compound of emperical formula HCdX. Cuprous chloride was shown to react with AlH_3 in ether at -78° to form CuH and $CuAlH_4$ both of which decompose when allowed to warm to room temperature. All compounds were characterized by X-ray powder diffraction, infrared spectroscopy and elemental analyses.

Introduction

In view of our recent study of the redistribution reaction of aluminum hydride with beryllium chloride in diethyl ether and the possibility of the existence of HMX compounds (where M = Groups II A and B metals and X = Cl, Br, or I), we have extended our investigation of redistribution reactions involving AlH_3 to include other Group II A and B metal halides in addition to $BeCl_2$ and $BeBr_2$.[1]

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \qquad (1)$$

(1) E. C. Ashby, P. Claudy and R. D. Schwartz, Inorg. Chem., 13, 192 (1974).

Although there have been several reports of the preparation and characterization of Groups II A and B metal hydrides in the literature,[2]

(2) E. Wiberg and E. Amberger, Hydrides of the Elements of Main Groups I-IV, Elsvier Publishing Company, 1971, pp. 48-80, 422 and references therein.

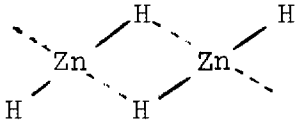
very little is known about the corresponding hydridometal halides (HMX). In 1951 Wiberg and Henle[3] reported that the addition of an ether

(3) E. Wiberg, Walter Henle and R. Bauer, Z. Naturforsch, 6b, 393 (1951).

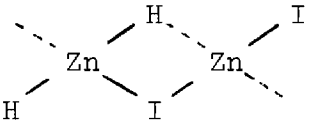
solution of zinc chloride to a solution of aluminum hydride and aluminum chloride (1:1 mole ratio) in ether produced impure zinc hydride. These workers also reported[4] the preparation of a white solid corresponding to

(4) E. Wiberg and Walter Henle, Z. Naturforsch, 7b, 249 (1952).

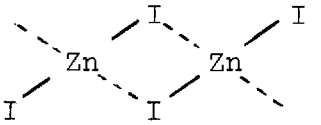
the formula HZnI by the reaction of zinc iodide with lithium hydride in diethyl ether. Since HZnI could not be isolated in pure form and contained different amounts of iodine, depending on the conditions of isolation; resonance structures (a, b, c,) were suggested to describe the compound.



(a)



(b)



(c)

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture[10] or on the bench using typical Schlenk-tube techniques.[11]

(10) E. C. Ashby and R. D. Schwartz, J. Chem. Ed., 51, 65 (1974).

(11) D. H. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, 1969.

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 621 Grating Infrared Spectrophotometer using NaCl and CsI liquid cells. Solid samples were prepared as mulls in nujol and the spectra were measured using polyethylene and CsI plates. X-ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46 cm diameter camera with Ni-filtered CuKα radiations. The samples were exposed for 6.0 hr. d-Spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA-TGA analyses were carried out using a Mettler Thermoanalyzer II with high vacuum attachment.[12]

(12) E. C.Ashby and Pierre Claudy, J. Chem. Ed., (in press).

Reagents. Diethyl ether (Fisher anhydrous ether) was distilled over $LiAlH_4$ immediately prior to use. All metal halides were Fisher Certified reagent grade. Aluminum halides were purified by vacuum sublimation and ether solutions were prepared at -20° by slow addition of

the aluminum halide to pre-cooled ether. An ether solution of $MgBr_2$ was obtained by the method described previously.[13]

(13) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

Zinc halides were dried by heating the compounds slowly with a Bunsen flame under vacuum until they sublimed completely. Ether solutions of $ZnBr_2$ were obtained by dissolving the sublimed material in ether at room temperature. Anhydrous $CdBr_2$ was dried further by heating at 115° overnight under vacuum. Ether soluble aluminum hydride was prepared by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether.[14] Caution! Special care must be taken while handling beryllium compounds due to their toxic character.

(14) E. C. Ashby, J. R. Sanders, P. Claudy and R. D. Schwartz, J. Amer. Chem. Soc., 95, 6485 (1973).

Analytical Procedures. Hydrogen analysis was carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexiметric titration with EDTA. Zinc, magnesium and cadmium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Analysis for chloride, bromide or iodide was carried out using a modified Volhard procedure.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ and $AlBr_3$ in Diethyl Ether. The hydridoaluminum halides, H_yAlX_{3-y} (where Y = Cl, or Br), were prepared by mixing solutions of AlH_3 and aluminum halides in ether at 0° in the appropriate ratios. Redistribution reactions between AlH_3 and aluminum halides have been discussied by a number of authors.[15] The

(15) E. Wiberg and M. Schmidt, Z. Naturforsch, 6b, 460 (1951); S. M. Arkhipov and V. I. Mikeeva, Zh. Neorg. Khim., 11, 2006 (1966); E.C. Ashby and J. Prather, J. Am. Chem. Soc., 88, 729 (1966).

infrared spectra are reported in Figure 1.

Reaction of AlH_3 with $MgBr_2$. (a) In 1:1 Mole Ratio. A solution of AlH_3 (10 ml, 2.732 mmoles) in ether was added slowly with stirring to a solution of $MgBr_2$ (21.45 ml, 2.732 mmoles) in ether. There was no immediate precipitate and the mixture remained clear even after 24 hours stirring. The infrared spectrum of the clear solution showed strong bands at 1785 cm^{-1} and 760 cm^{-1} and a band of medium intensity at 380 cm^{-1}. The infrared spectrum of the solid obtained by complete removal of ether from the reaction mixture showed bands at 1800 (w) and 1600 cm^{-1} (br,s). Elemental analysis of the solid gave the ratio Mg:Al:H:Br = 1.0: 1.04:2.90:2.11. X-ray powder diffraction patterns of the solid showed it to be essentially a physical mixture of $MgBr_2$ and AlH_3. When the reaction mixture was allowed to stand for a few weeks, some grey solid compound precipitated. The solid was filtered, dried under vacuum and analyzed: Mg:Al:H:Br = 1.24:1.0:1.02:1.95. The infrared spectrum showed a very weak broad band at ~ 1600 cm^{-1}.

(b) In 1:2 Mole Ratio. Ether solutions of AlH_3 (8.578 mmoles) and $MgBr_2$ (4.289 mmoles) were mixed as described above. In this case also there was no immediate precipitate and the mixture stayed clear for more than 24 hr. The infrared spectra of the clear mixture and the solid obtained after complete removal of ether, were identical with the spectra obtained in (a). Similarly X-ray powder patterns from (a) and (b) were identical. In this case, however, it was noticed that the formation of

grey solid compound was faster than in (a) and in one week 33% of the solid (calculated on the basis of solid $MgBr_2 \cdot AlH_3$) precipitated from solution. Analysis of the grey powder showed: Mg:Al:H:Br = 1.0:1.70:2.22:1.41.

Reaction of AlH_3 with $ZnCl_2$. Preparation of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$. In a typical reaction, a solution of aluminum hydride in ether was added slowly to a solution of zinc chloride in ether in an appropriate ratio (see below). An immediate precipitatation of a white solid took place. The mixture was stirred for ten minutes and then filtered. The white residue was washed with ether, dried under vacuum and stored at -20°. Anal. Calcd. for $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$: Zn, 66.99; H (hydrolysable), 1.57; Cl, 18.16. Found: Zn, 66.52; H (hydrolysable), 1.59; Cl, 17.82. The yield of product based on this analysis was 95%. The infrared spectrum of the white solid showed a very broad band with a maximum at ~ 1550 cm^{-1} and a weak band at ~ 460 cm^{-1}. The X-ray powder diffraction data given in Table 1 showed lines different from $ZnCl_2$ and AlH_3.

The reaction was repeated in the following ratios of AlH_3:$ZnCl_2$; 1:1, 1:2, 1:3 and 4:1. The white precipitate obtained in each case was subjected to complete elemental analysis and characterized by infrared spectra and X-ray powder diffraction. Similarly, the filtrate after isolation of the white solid, was characterized by infrared spectroscopy and elemental analysis. The results are described separately.

(a) In 1:1 Mole Ratio. Aluminum hydride, 6.75 mmoles in ether solvent was mixed with zinc chloride, 6.75 mmoles in ether solvent. Analysis of the resulting white solid gave Al:Zn:H:Cl = 0.07:1.00:1.74:0.41. Infrared analysis of the solid (nujol mull) showed two broad bands at ~ 1550 and 600-350 cm^{-1} centered at 460 cm^{-1}. The X-ray powder pattern of the solid was different from the patterns obtained for $ZnCl_2$ and AlH_3

(Table 1). Elemental analysis of the filtrate showed: H:Al:Cl:Zn = 1.60:1.00:1.57:0.00 and infrared analysis showed the following bands: 1898 (s), 1850 (ms), 775 (s) and 720 (s) cm^{-1}.

(b) In 1:2 Mole Ratio. AlH_3, 6.846 mmoles in ether solvent, was mixed with $ZnCl_2$, 13.692 mmoles in ether solvent. Elemental analysis of the solid residue showed: Al:Zn:H:Cl = 0.05:1.00:1.56:0.486. The infrared spectrum and X-ray powder diffraction pattern were similar to the solid described earlier (a). The infrared spectrum of the filtrate did not show any bands between 2000 - 1600 cm^{-1} and 800 - 700 cm^{-1}.

(c) In 1:3 Mole Ratio. AlH_3, 2.259 mmoles in ether solvent was mixed with 6.779 mmoles of $ZnCl_2$ in ether solvent. Analysis of the resulting precipitate gave Al:Zn:H:Cl = 0.00:1.00:1.49:0.57. An infrared spectrum and X-ray powder pattern were obtained as in the previous cases. The analysis of the filtrate showed Al:Zn:Cl:H = 1.00:0.64:3.98:0.00. Infrared analysis did not show any absorption bands due to a hydrido-aluminum halide.

(d) In 4:1 Mole Ratio. AlH_3, 5.957 mmoles in ether solvent was mixed with 1.489 mmoles of $ZnCl_2$ in ether solvent. Analysis of the resulting white precipitate gave Al:Zn:H:Cl = 0.07:1.00:1.91:0.43. The infrared spectrum of the filtrate showed strong bands at 1900, 1850 (sh), 1785 and 760 cm^{-1}.

Reaction of $HAlCl_2$ with $ZnCl_2$. 40 ml (7.404 mmoles) of $HAlCl_2$ solution in ether was added slowly to a solution of zinc chloride (21.8 ml, 7.404 mmoles) in ether. There was an immediate precipitation of a white solid. The mixture was stirred for about ten minutes and then filtered. The residue was washed, dried under vacuum and analyzed: Al:Zn:H:Cl: = 0.12:1.00:1.40:0.76. The infrared spectrum of the filtrate showed a broad band near 1500 - 1400 cm^{-1}.

Reaction of AlH_3 with $ZnBr_2$. Preparation of $H_3Zn_2Br \cdot 0.29(C_2H_5)_2O$. A solution of aluminum hydride was added slowly with stirring to a solution of zinc bromide in ether and the mixture stirred about ten minutes. The white solid was filtered, washed with ether and dried under vacuum. The compound was stored at -20°. Anal. Calcd. for $H_3Zn_2Br \cdot 0.29(C_2H_5)_2O$: H(hydrolysable) , 1.28; Zn, 55.51; Br, 33.93. Found: H (hydrolysable), 1.17; Zn, 61.42; Br, 26.58. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1}. X-ray powder diffraction data is given in Table 1. The above reaction was carried out in several mole ratios of AlH_3:$ZnBr_2$ and the results are described below.

(a) In 1:1 Mole Ratio. AlH_3, 6.357 mmoles in ether solvent was added to $ZnBr_2$, 6.357 mmoles in ether solvent. A white solid precipitated and was analyzed: Al:Zn:H:Br = 0.03:1.00:1.91:0.37. Infrared analysis of the solid (nujol mull) showed a broad band near 1600 cm^{-1}. The infrared spectrum of the filtrate showed the following bands: 1900 (s), 1850 (sh), 765 (s) and 700 cm^{-1} (ms). The filtrate on standing overnight at room temperature deposited some grey powder which was mostly metallic zinc.

(b) In 1:2 Mole Ratio. AlH_3, 5.495 mmoles in ether solvent was added to $ZnBr_2$, 10.99 mmoles in ether solvent. Elemental analysis of the resulting solid gave Al:Zn:H:Br = 0.04:1.01:1.66:0.36. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1} whereas the infrared spectrum of the filtrate did not show any band between 2000 - 1600 cm^{-1} and between 800 - 700 cm^{-1}.

(c) In 1:3 Mole Ratio. AlH_3, 7.334 mmoles in ether solvent was mixed with $ZnBr_2$, 22.00 mmoles in ether solvent. Analysis of the white precipitate gave the molar ratio: Al:Zn:H:Br = 0.04:1.00:2.06:0.41. The infrared spectrum of the filtrate did not show any absorption band due to hydridoaluminum compounds.

Reaction of AlH_3 with ZnI_2. Preparation of $ZnI_2 \cdot AlH_3 \cdot 1.79(C_2H_5)_2O$. Solutions of aluminum hydride and zinc iodide in ether solvent were allowed to react. The white solid which precipitated immediately after mixing was filtered, washed with ether, dried under vacuum and stored at -20°. Anal. Calcd. for $ZnI_2 \cdot AlH_3$, $1.79(C_2H_5)_2O$. Zn, 13.55; I, 52.64; Al, 5.59; H (hydrolysable), 0.627. Found: Zn, 13.86; I, 53.07; Al, 5.99: H (hydrolysable), 0.693. The infrared spectrum of the white solid showed the following bands in addition to bands due to diethyl ether: 1630 (vs, br), 670 (s), 520 (m) and 325 cm^{-1} (w). The X-ray powder diffraction pattern of the solid is listed in Table 1. The reaction was carried out in several mole ratios of AlH_3:ZnI_2 and the results are described below.

(a) In 1:2 Mole Ratio. AlH_3, 1.473 mmoles in ether solvent was mixed with ZnI_2, 2.947 mmoles in ether solvent. Analysis of the white solid precipitate gave a molar ratio of Zn:Al:H:I = 1.0:1.07:2.99:1.97. An infrared spectrum and X-ray powder diffraction pattern were identical with those described for the reaction carried out in 1:1 ratio. Analysis of the filtrate showed: Al:Zn:H:I = 0.09:1.00:0.04:2.12. An infrared spectrum of the filtrate did not show any absorption bands near 2000-1600 cm^{-1} and 800-700 cm^{-1}. In a separate experiment, ether solutions of AlH_3 and ZnI_2 were mixed together in 1:2 mole ratio and the mixture was stirred at 0° for two days. The white solid was then filtered, washed with ether and dried under vacuum. The elemental analysis and the infrared spectrum of the white solid were identical to that described above.

(b) In 4:1 Mole Ratio. AlH_3, 5.825 mmoles in ether solvent was mixed with ZnI_2, 1.453 mmoles in ether solvent. A white solid which precipitated immediately after mixing showed a molar ratio of Al:Zn:H:I = 1.04:1.00:3.26:1.91. The infrared spectrum and X-ray powder diffraction

data were identical to that described above. However, the infrared spectrum of the filtrate showed absorption bands at 1785 (s) and 760 cm^{-1} (s).

Reaction of AlH_3 with $CaBr_2$. A solution of aluminum hydride (20.1 ml, 4.794 mmoles) in diethyl ether was added to a slurry of $CaBr_2$ (0.9583 g, 4.794 mmoles) in 100 ml ether. The mixture was stirred for three days at room temperature. It was then filtered, washed with ether and the residue dried under vacuum. Elemental analysis of the residue gave: Ca:H:Br = 1.00:0.02:1.97. An infrared spectrum of the filtrate showed bands due to aluminum hydride only at 1785 (s) and 760 cm^{-1} (s).

Reaction of AlH_3 with $CdBr_2$. 1.9495 g (7.161 mmoles) of $CdBr_2$ was transferred to a 250 ml Schlenk tube followed by the addition of 50 ml of diethyl ether. The mixture was stirred at -40° to -30° for about fifteen minutes and then a solution of aluminum hydride (26.0 ml, 7.161 mmoles) in diethyl ether was added to the $CdBr_2$ slurry dropwise keeping the temperature of the reaction mixture always below -30°. The mixture was stirred for four days at -40 to -30° during which time infrared spectra of the clear solution were recorded in order to follow the progress of the reaction. When the reaction was complete, a small portion of the solution was analyzed: Al:Cd:H:Br = 1.00:0.00:2.12:0.79. The infrared spectrum of the filtrate showed bands at 1860 (s, br), 760 (s) and 700 cm^{-1} (s). The solid residue (slightly grey) was washed twice with cold (-70°) ether allowing the precipitate to settle to the bottom of the Schlenk tube while removing the clear liquid by syringe under nitrogen. The solid was analysed: Cd:H:Br = 1.00:1.00:1.14. Hydrogen analysis was carried out by attaching the Schlenk tube with the solid directly to the vacuum line and allowing the solid to decompose at room temperature.

The above reaction was studied in detail under the following conditions.

(a) Reaction Product Allowed to Warm to Room Temperature. $CdBr_2$ and AlH_3 were mixed in 1:1 mole ratio in diethyl ether in the same way as described above. The mixture was stirred for 6 hr at -78° and then allowed to warm slowly to room temperature. When the temperature of the reaction mixture reached -20°, it started turning dark and at room temperature became completely black giving off hydrogen gas. The black solid was separated by filtration, washed with ether and dried under vacuum. The infrared spectrum of the solid did not show any absorption bands due to metal hydrides. The infrared spectrum of the filtrate on concentration showed bands at 1906 (s), 762 (s) and 700 cm^{-1} (s). Analysis of the filtrate showed: Al:H:Br = 1.00:0.576:2.00 and it contained 73% of the total aluminum. Elemental Analysis of the black residue gave: Al:Cd:H:Br = 0.08:1.00:0.00:1.73.

(b) Reaction in THF. Since $CdBr_2$ is more soluble in THF than diethyl ether, a solution of AlH_3 (3.3 ml, 1.320 mmoles) in THF was added to a solution of $CdBr_2$ (200 ml, 1.320 mmoles) in THF at -78°. The mixture was stirred at -35° for 4 hr and then allowed to settle overnight inside a dewar flask. It was noticed that even after 16 hr the mixture remained turbid. The supernatent liquid was then removed carefully, with a syringe and the remaining solid washed with cold THF. The resulting solid was analyzed: Al:Cd:H:Br = 0.93:1.00:1.00:2.09.

(3) Reaction in 3:1 Mole Ratio in Ether. $CdBr_2$ and AlH_3 were mixed in 3:1 mole ratio in ether and the mixture stirred for 6 hr at -40 to -35°. The mixture was allowed to settle and the infrared spectrum of the clear solution showed the absence of any hydridoaluminum compound. The reaction mixture was then cooled to -76° and transferred inside the glove box as

fast as possible flushing the entryport with nitrogen for ten minutes. It was then filtered and washed with cold (-40°) ether. The white solid residue turned black within a few seconds. The infrared spectrum of the filtrate on concentration did not show any absorption bands due to aluminum-hydrogen compounds. Analysis of the filtrate showed: H:Al:Cd:Br = 0.00: 1.00:0.00:0.76, corresponding to 36.2% of the total aluminum.

Reaction of H_2AlBr with $CdBr_2$ in Ether. 61 ml (7.585 mmoles) of H_2AlBr in ether was added to a slurry of $CdBr_2$ (2.0649 g, 7.585 mmoles) in ether stirred at -40°. The mixture was stirred for five days at -40 to -30° until the reaction was complete. The infrared spectrum of the clear solution showed a strong and broad band at 1900 - 1800 cm^{-1} with a maximum at 1850 cm^{-1}. The position of the band did not change on further stirring. Analysis of the solution showed: Al:Cd:H:Br = 1.00:0.04:1.90: 1.15, whereas the analysis of the residue on decomposition at room temperature and subsequent hydrolysis gave: Al:Cd:H:Br = 0.09:1.00:0.19: 1.94.

Reaction of AlH_3 with CuCl in Ether. 42.7 ml (12.89 mmoles) of aluminum hydride solution in ether was added to a slurry of CuCl (1.276 g, 12.89 mmoles) in ether. The mixture was stirred for 6 hr at -76° and then allowed to warm to room temperature. At -40°, the color of the reaction mixture started to turn black and by the time the temperature rose to 0°, it was almost completely black giving off some gas and depositing a black precipitate at the bottom of the flask. It was then filtered, washed with ether and the residue dried at room temperature. The infrared spectrum of the filtrate showed a strong band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1}, and a strong band at 775 cm^{-1}. Analysis of the filtrate gave a molar ratio of Al:H:Cl = 1.04:1.00:1.80 corresponding to 44.2% of the total aluminum.

Results and Discussion

The reaction of aluminum hydride with Groups I and II A and B metal halides can be considered as a metathetical exchange reaction in which one or more hydrogen atoms of alane are exchanged with the halogen atom of the metal halide. The electronegativity differences for metal halides are calculated from the expression (eq. 2) were Q = standard heat

$$Q = 23 \Sigma (X_A - X_B)^2 \qquad (2)$$

of formation and $X_A - X_B$ = electronegativity difference for the elements A and B.[16] The electronegativity differences for metal halides are

(16) L. Pauling, The Nature of The Chemical Bond, Cornell University Press, Ithaca, New York, 1960, p. 92.

listed in Table II. A comparison of the electronegativity differences with the experimental observations show that if the electronegativity of the Group I or II metal is higher than aluminum, the exchange reaction does not take place. However, in the case of comparable or lower electronegativity differences the exchange does take place. This simply means that in the exchange reaction between AlH_3 and metal halide the reaction will proceed to form the most thermodynamically stable products which are those resulting from the most electronegative group (halogen) residing on the most electropositive metal. Therefore, AlH_3 would not be expected to react with LiCl to form $AlCl_3$ and LiH, but would be expected to react with $ZnBr_2$ to form $AlBr_3$ and ZnH_2.

As reported previously,[14] redistribution reactions are studied by mixing ether solutions of metal hydrides with metal halides in various

mole ratios followed by complete elemental analysis of the resulting solution and precipitate that forms. The precipitate is further analyzed by X-ray powder diffraction, DTA-TGA and infrared analysis whereas the solutions are analyzed further only by infrared spectroscopy.

Reactions of AlH_3 with AlX_3 (where X = Cl and Br). Since hydrogen exchange in the AlH_3-MX_2 system would be expected to form hydridoaluminum halides, it was necessary first to prepare $HAlX_2$ and H_2AlX (where X = Cl and Br) in order to obtain the necessary infrared spectroscopic information for indentification purposes. Ether soluble AlH_3 was found to exhibit bands in its infrared spectrum at 1785 and 770 cm^{-1}. These bands are assigned to the Al-H stretching and Al-H deformation vibrations, respectively. The hydridoaluminum halides (where X = Cl and Br) were prepared in ether solvent by simply mixing ether solutions of AlH_3 and the appropriate aluminum halide at low temperature in order to avoid ether cleavage. The infrared spectra are recorded in Figures 1 and 2.

$$2\ AlH_3 + AlH_3 \rightarrow 3\ AlH_2X \qquad (3)$$

$$AlH_3 + 2\ AlX_3 \rightarrow 3\ AlHX_2 \qquad (4)$$

Reactions of AlH_3 with $CdBr_2$. Calcium bromide does not undergo an exchange reaction with AlH_3 due to the fact that calcium is more electropositive than aluminum. Elemental analysis as well as the infrared analysis of the products obtained after mixing an ether solution of AlH_3 with $CaBr_2$ result in a quantitative recovery of unreacted calcium bromide and AlH_3.

Reactions of AlH_3 with $MgBr_2$. Similarly, $MgBr_2$ does not react with AlH_3 in diethyl ether. Although there is no immediate precipitate after mixing an ether solution of $MgBr_2$ with AlH_3, the possibility of some soluble complex metal hydride could not be ruled out completely. Therefore, in order to isolate and characterize any possible complex, the infrared spectrum of magnesium bromide and AlH_3 were determined in the near and far infrared regions in order to establish metal-hydrogen (deformation) and metal-halogen stretching frequencies. The infrared spectra of both $MgBr_2$ and the reaction mixture showed only one medium intense band at 380 cm^{-1} other than weak bands for diethyl ether (Figure 3). This band may be assigned to the Mg-Br stretching vibration. Powder diffraction patterns were obtained for $MgBr_2$ and AlH_3 containing nearly the same number of solvent molecules (Table 1) as that of the product after solvent removal. The X-ray powder pattern of the product was consistent with a physical mixture of $MgBr_2$ and AlH_3. Similarly, the TGA analysis of the solid showed it to be either a very weak complex of AlH_3 or AlH_3 diethyl etherate mixed with $MgBr_2$. On standing for several days at room temperature the reaction mixture decomposed to hydrogen and aluminum which precipitated as a grey powder. The absence of infrared absorption bands characteristic of the Mg-H stretching vibration ruled out the possibility of the existence of either MgH_2 or HMgBr in the grey solid.

Reactions of $ZnCl_2$ with AlH_3. In 1:1 mole ratio $ZnCl_2$ and AlH_3 react to produce a stable white solid of empirical formula $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$.[17] The infrared spectrum of the filtrate showed

(17) The ether content of this compound is a result of drying the compound under vacuum for one hour before analysis. Further attempts to remove additional solvent by subjecting to vacuum for a longer period of time resulted in decomposition of the solid.

absorption bands at 1900 (s), 1850 (s), 780 (s) and 720 cm^{-1} (s), indicating the presence of $HAlCl_2$ and H_2AlCl in solution. These results suggest that the reaction takes place in the following manner:

$$2\ ZnCl_2 + 2\ AlH_3 \rightarrow 2\ H_2AlCl + 2\ HZnCl \quad (5)$$

$$H_2AlCl + HZnCl \rightarrow ZnH_2 + HAlCl_2 \quad (6)$$

$$ZnH_2 + HZnCl \rightarrow H_3Zn_2Cl$$

$$2\ ZnCl_2 + 2\ AlH_3 \rightarrow H_3Zn_2Cl + H_2AlCl + HAlCl_2 \quad (7)$$

The infrared spectrum as well as the X-ray powder diffraction pattern of the solid product shows it to be a unique compound and not a physical mixture of $ZnCl_2$ and ZnH_2. The infrared spectra of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$, $ZnCl_2 \cdot 0.11Et_2O$ and $ZnCl_2$ in the solid state are reported in Figure 4 and the X-ray powder diffraction patterns are listed in Table I. An X-ray powder diffraction pattern of $ZnCl_2 \cdot 0.35(C_2H_5)_2O$ could not be obtained because the solid was quite sticky. Possibly the most convincing piece of information suggesting that H_3Zn_2Cl is a single compound and not a mixture of ZnH_2 and $ZnCl_2$ in 3:1 ratio is the fact that $ZnCl_2$ is soluble in ether, yet the H_3Zn_2Cl ratio is maintained under a variety of conditions.

In 2:1 mole ratio, $ZnCl_2$ and AlH_3 reacted to yield the same solid

compound, $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$ which was characterized by elemental analysis, X-ray powder diffraction and infrared analysis. However, the infrared spectrum and elemental analysis of the filtrate showed it to contain only $AlCl_3$ indicating the following sequence of reactions:

$$2\ ZnCl_2 + AlH_3 \rightarrow 2\ HZnCl + HAlCl_2 \qquad (8)$$

$$HZnCl + HAlCl_2 \rightarrow ZnH_2 + AlCl_3 \qquad (9)$$

$$ZnH_2 + HZnCl \rightarrow H_3ZnCl \qquad (10)$$

$$2\ ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + AlCl_3 \qquad (11)$$

The infrared spectrum and elemental analysis of the solid compound obtained by reacting $ZnCl_2$ and AlH_3 in 3:1 mole ratio showed the solid product to be $H_3Zn_2Cl \cdot 0.38(C_2H_5)_2O$; however, the filtrate contained 1 mole of $AlCl_3$ as well as 1 mole of unreacted $ZnCl_2$ as expected from the results described by equation 12.

$$3\ ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + ZnCl_2 + AlCl_3 \qquad (12)$$

When $ZnCl_2$ and AlH_3 were allowed to react in 1:4 mole ratio, $H_3Zn_2Cl \cdot 0.31Et_2O$ was again obtained, however the elemental analysis gave a molar ratio of Al:Zn:H:Cl = 0.07:1.00:1.91:0.43. The high hydrogen ratio indicates that in the presence of excess AlH_3 some HZnCl reacts further with AlH_3 to form ZnH_2 rather than complex with ZnH_2 already present to form H_3Zn_2Cl. Thus, the H_3Zn_2Cl formed is contaminated with ZnH_2.

In an attempt to verify the existence of HZnCl, zinc chloride and $HAlCl_2$ were allowed to react in 1:1 mole ratio in diethyl ether.

In this case a white solid was obtained corresponding to a molar ratio of Al:Zn:H:Cl = 0.12:1.00:1.40:0.76 suggesting the formation of H_3Zn_2Cl.

$$4\ ZnCl_2 + 4\ HAlCl_2 \rightarrow 4\ HZnCl + 4\ AlCl_3 \quad (13)$$

$$2\ HZnCl \rightarrow ZnH_2 + ZnCl_2 \quad (14)$$

$$HZnCl + ZnH_2 \rightarrow H_3Zn_2Cl \quad (15)$$

$$HZnCl \rightarrow 1/2\ ZnH_2 + 1/2\ ZnCl_2 \quad (16)$$

$$4\ ZnCl_2 + 4\ HAlCl_2 \rightarrow H_3Zn_2Cl + 1/2\ ZnH_2 + 3/2\ ZnCl_2 + AlCl_3 \quad (17)$$

Unfortunately HZnCl was not isolated as anticipated according to eq. 13. This means that either HZnCl reacts more rapidly with $HAlCl_2$ than $ZnCl_2$ to form ZnH_2 or that HZnCl disproportionates according to eq. 14. Either was ZnH_2 is formed which then complexes HZnCl to form the apparently stable H_3Zn_2Cl.

Reactions of $ZnBr_2$ with AlH_3. Like $ZnCl_2$, $ZnBr_2$ was also allowed to react with AlH_3 in 1:1 and 2:1 mole ratios in ether. As in the previous case a white solid was formed closely corresponding to the empirical formula $H_3Zn_2Br \cdot 0.29Et_2O$. However, H_3Zn_2Br appears to be less stable than H_3Zn_2Cl since the white solid decomposed (producing a light grey solid) rapidly when the reaction mixture was stirred for the same period of time at room temperature. The light grey color is presumably due to the formation of zinc metal. The reactions were in general comparable with the reactions of $ZnCl_2$ with AlH_3. X-ray powder diffraction patterns for $ZnBr_2$, $ZnBr_2 \cdot 0.28Et_2O$ and $H_3Zn_2Br \cdot 0.29Et_2O$ are shown in Table 1. The fact that $ZnBr_2$ is soluble in ether and yet

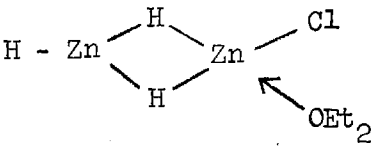
H_3Zn_2Br precipitated indicates that H_3Zn_2Br cannot be a mixture of ZnH_2 and $ZnBr_2$ in 3:1 ratio.

Reactions of ZnI_2 with AlH_3. In 2:1 mole ratio, ZnI_2 and AlH_3 in diethyl ether react to yield a white solid corresponding to the composition $ZnI_2 \cdot AlH_3 \cdot 1.79Et_2O$. Infrared analysis and X-ray powder diffraction of the solid compound showed it to be different from a physical mixture of ZnI_2 and AlH_3. The infrared spectrum as well as elemental analysis of the filtrate did not show the presence of any hydridoaluminum halides. Similarly, when the reaction was carried out in 1:4 mole ratio (ZnI_2:AlH_3), a white solid resulted having the same composition. An infrared spectrum of the filtrate showed absorption bands due to AlH_3 alone. Therefore, it is safe to conclude that zinc iodide and AlH_3 in all stoichiometric ratios react to form $ZnI_2 \cdot AlH_3 \cdot n\ Et_2O$.

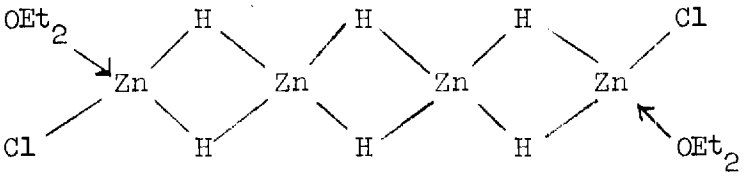
$$ZnI_2 + AlH_3 \rightarrow ZnI_2 \cdot AlH_3 \qquad (18)$$

Very little can be said about the structures of the new zinc-hydrogen compounds (H_3Zn_2Cl, H_3Zn_2Br, $ZnI_2 \cdot AlH_3$) prepared in this study. If the compounds were soluble in some solvent, molecular weight and infrared studies could reveal much structural information. However, all of the hydrides were insoluble in all solvents in which they were tested leaving only single crystal X-ray diffraction studies as a source of further information. In any case it might be worthwhile to point out at least some of the structural possibilities that should be considered for H_3Zn_2Cl.

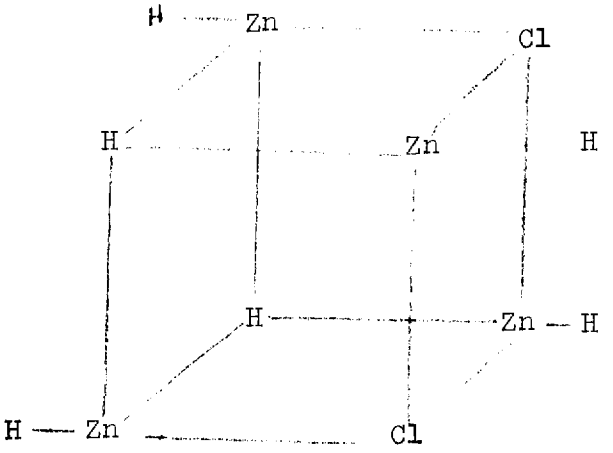
(1)



(2)



(3)



Reactions of $CdBr_2$ with AlH_3. In 1:1 mole ratio, $CdBr_2$ and AlH_3 in diethyl ether were allowed to react at -40° to -30° for 40 hr with stirring to yield a slightly grey solid which exhibited a molar ratio of Cd:H:Br = 1.00:1.00:1.143. The solid decomposed to Cd, H_2 and $CdBr_2$ slowly at -20° and more rapidly at room temperature. As reported earlier by Wiberg and Henle,[2] CdH_2 was also found to decompose at -20°. Therefore, although the elemental analysis of the solid compound suggest the formation of HCdBr compound, the possibility of a physical mixture of CdH_2 and $CdBr_2$ cannot be ruled out. Elemental analysis of the filtrate showed the presence of H_2AlBr which was also supported by an infrared spectrum which exhibited bands characteristic of H_2AlBr.

In order to establish the nature of the solid product as HCdBr (eq. 19) and not a mixture of $CdBr_2$ and CdH_2 (eq. 20), an attempt was made to allow a mixture of $CdBr_2$ and H_2AlBr to react in diethyl ether in 1:1 ratio at -40°. If the reaction of $CdBr_2$ and AlH_3 proceeds according to eq. 20, then $CdBr_2$ is produced in the presence of H_2AlBr. Since it is possible that $CdBr_2$ is reduced in the presence of H_2AlBr (eq. 21), the presence of $HAlBr_2$ would indicate the presence of $CdBr_2$ in solution. If indeed this reaction occurs (eq. 21) this would indicate the absence of $CdBr_2$ in the reaction product of $CdBr_2$ and AlH_3, thus eleminating eq. 20 as the reaction course. Unfortunately, no reaction took place; thus,

$$CdBr_2 + AlH_3 \rightarrow HCdBr + H_2AlBr \qquad (19)$$

$$CdBr_2 + AlH_3 \rightarrow \boxed{1/2\ CdH_2 + 1/2\ CdBr_2} + H_2AlBr \qquad (20)$$

$$CdBr_2 + H_2AlBr \rightarrow HCdBr + HAlBr_2 \qquad (21)$$

it is not possible to tell whether the reaction product is HCdBr or a physical mixture of $CdBr_2$ and CdH_2.

Because of the low solubility of $CdBr_2$ in diethyl ether, an attempt was also made to study the reaction in THF; however, the reaction was found to be too slow at -40 to -30° and the reaction product decomposed above -20°.

Reactions of CuCl with AlH_3. When cuprous chloride and AlH_3 were allowed to react in 1:1 mole ratio in ether at -78° and then allowed to warm slowly to room temperature, the reaction mixture turned completely black giving off a gas. The elemental analysis as well as an infrared spectrum of the filtrate suggests that the reaction takes place according to the following reaction sequence:

$$CuCl + AlH_3 \rightarrow CuH + H_2AlCl \quad (22)$$

$$CuCl + H_2AlCl \rightarrow CuH + HAlCl_2 \quad (23)$$

$$CuH + AlH_3 \rightarrow CuAlH_4 \quad (24)$$

$$2\ CuCl + 2\ AlH_3 \rightarrow CuH + CuAlH_4 + HAlCl_2 \quad (25)$$

The infrared spectrum of the filtrate showed a sharp band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1}. Elemental analysis of the filtrate indicated only 43% of the total aluminum. The infrared spectrum of the black solid product did not show any absorption bands due to either hydridoaluminum compounds or hydridocopper compounds. Thus, it appears that the black solid product is a mixture of copper and aluminum metal formed according to equation 26. Since the filtrate was shown to be an

$$CuH + CuAlH_4 \rightarrow 2\ Cu + Al + 5/6\ H_2 \quad (26)$$

ether solution of $HAlCl_2$ and since half of the aluminum was in the filtrate and half in the precipitate, it appears that there is ample data to suggest the above reaction sequence.

Acknowledgement. We wish to acknowledge financial support of this by the Office of Naval Research. Grant No. N-14-67-A-0159-005

Table I. X-Ray Powder Pattern d-Spacing Data

$MgBr_2 \cdot 0.89Et_2O$		$MgBr_2 + AlH_3 \cdot 1.24Et_2O$		$MgBr_2 + 2\ AlH_3 \cdot 1.62Et_2O$	
d,A	I/IO	d,A	I/IO	d,A	I/IO
9.25	vw	9.50	w	9.50	s,br
8.0	s	8.0	s	8.25	w
7.25	s	7.25	s	7.25	w
5.8	m	5.7	vvw	6.6	w
5.4	m	5.4	m	5.90	w
4.8	s	4.8	vvw	5.4	vvw
3.95	vw	3.95	vw	4.6	vw
3.72	vvw	3.55	ms	3.62	w
3.55	s	3.25	ms	3.50	w
3.25	s	2.97	w	3.25	m
3.01	ms	2.75	w	3.15	s
2.77	s	2.63	w	2.72	ms
2.75	w	2.52	w	2.63	vvw
2.64	w	2.36	w	1.92	s
2.52	m	2.25	vw	1.65	ms
2.42	w	2.125	vw	1.58	vw
2.36	w	1.91	ms	1.255	w
2.25	vw	1.71	w	1.223	w
2.19	m				
1.91	w				
1.75	w				
1.61	w				
1.53	w				
1.440	w				

Table 1 Continued

ZnI_2		$ZnCl_2$		$ZnCl_2 \cdot 0.1 Et_2O$		$H_3Zn_2Cl \cdot 0.2 Et_2O$	
d,A	I/I_0	d,A	I/I_0	d,A	I/I_0	d,A	I/I_0
4.51	vw	4.85	s	6.85	m	7.8	s
4.23	s	4.70	s	5.50	m	5.80	w
3.80	vw	3.80	w	4.80	s	5.40	w
3.40	m	3.26	m	4.50	m	4.0	m
2.97	vw	3.19	m	3.80	vw	3.55	w
2.82	vw	3.02	s	3.55	m	3.15	w
2.608	w	2.87	s	3.42	w	2.75	s
2.468	vw	2.85	w	3.30	w	2.65	s
2.387	m	2.35	w	3.05	s	2.37	m
2.290	m	2.22	w	2.87	m	2.00	w
2.225	m	2.12	vw	2.57	w	1.79	vw
2.135	w	1.960	vw	2.35	m	1.69	w
2.085	w	1.920	m	2.20	m	1.58	m
2.017	vw	1.860	s	2.06	w	1.55	w
1.905	w	1.730	s	1.97	w	1.51	w
1.764	w	1.620	w	1.95	m		
1.688	vw	1.592	s	1.865	s		
1.630	vw	1.490	w	1.730	m		
1.562	vw	1.455	w	1.620	m		
1.486	vw	1.280	vw	1.590	w		
1.464	vw	1.265	vw	1.570	m		
1.416	vw	1.145	vw	1.485	vw		
		1.350	vw	1.350	vw		
		1.265	vw	1.265	vw		
		1.215	vw	1.215	vw		
		1.095	vw	1.095	vw		

Table I Continued

$ZnBr_2 \cdot 0.286Et_2O$		$H_3Zn_2Br \cdot 0.29Et_2O$	
d,A	I/I_0	d,A[+]	I/I_0
6.5	vvw	10.0	w,br
4.2	w	3.5	w,br
3.4	s		
2.80	vvw		
2.55	vw		
1.99	m		
1.95	s		
1.70	m		
1.64	w		
1.27	w		
1.150	vw		

$AlH_3 \cdot 0.35Et_2O$		ZnI_2		$ZnI_2 \cdot 0.35Et_2O$		$ZnI_2AlH_3 \cdot 0.192\ Et_2O$	
d,A	I/I_0	d,A	I/I_0	d,A	I/I_0	d,A	I/I_0
11.5	s	3.45	s	3.45	s	8.80	m
4.55	m	3.05	w	3.05	vw	7.00	m
3.85	m	2.17	w	2.17	vw	5.40	vw
2.85	m	2.12	m	2.12	m	4.90	w
2.32	m	1.84	m	1.84	m	4.35	w
		1.78	w	1.78	w	3.95	w
		1.37	vw	1.375	vw	3.4	s
		1.235	vw	1.245	vw		

[+]Powder diffraction lines were obtained as two broad halos and these are only approximate distances.

Table II. Electronegativities of Elements and Electronegativity Difference Between the Metal and Halogen.

Elements	Electronegativity	Metal Halide	Electronegativity Difference
Ca	1.04	$CaBr_2$	1.87
Mg	1.23	$MgBr_2$	1.64
Be	1.47	$BeCl_2$	1.56
Al	1.47	$AlCl_3$	1.55
Zn	1.66	$ZnCl_2$	1.47
Cd	1.70	$AlBr_3$	1.35
Cu	1.90	$ZnBr_2$	1.30
H	2.20	$CdBr_2$	1.27
I	2.5	CuCl	1.18
Br	2.8	AlI_3	1.04
Cl	3.0	ZnI_2	1.04

Figure I. Infrared study of the reaction of AlH_3 with $AlCl_3$ in diethyl ether. I. AlH_3 2. AlH_2Cl 3. $AlHCl_2$

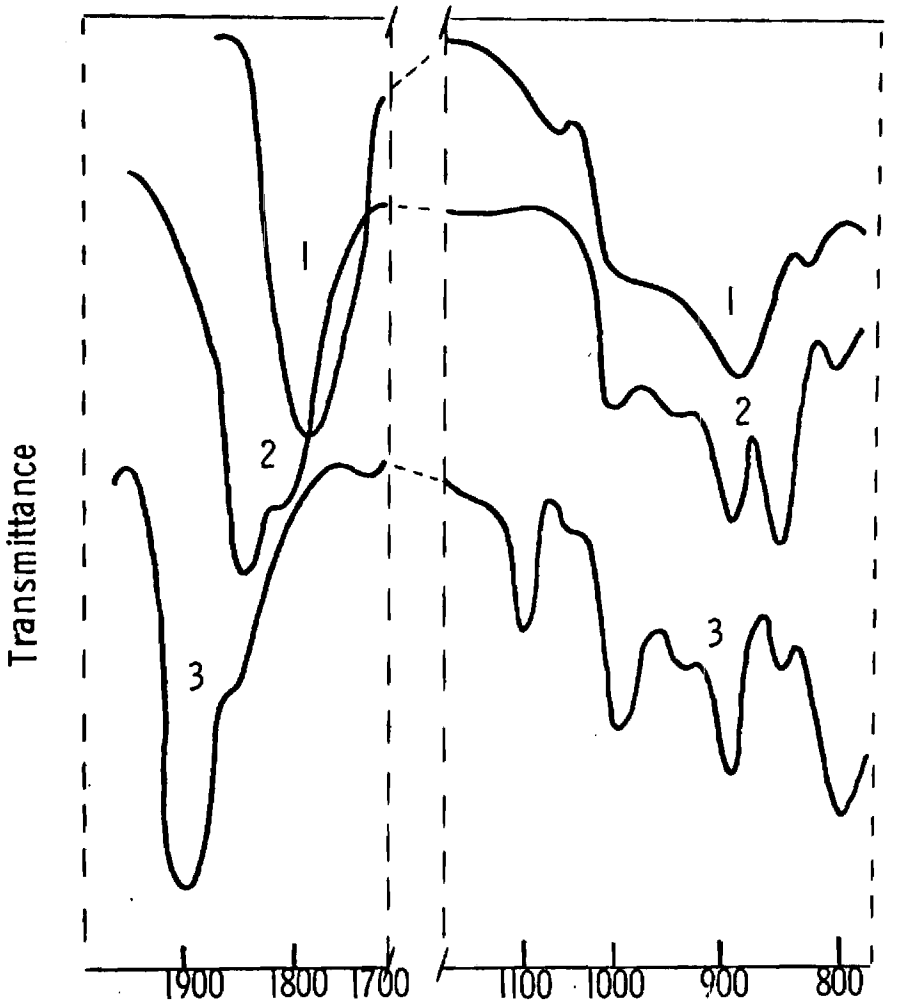

Transmittance
1
2
3
1
2
3
1900
1800
1700
1100
1000
900
800

Figure 2. Infrared spectra of AlH_3, H_2AlBr and $HAlBr_2$ in diethyl ether

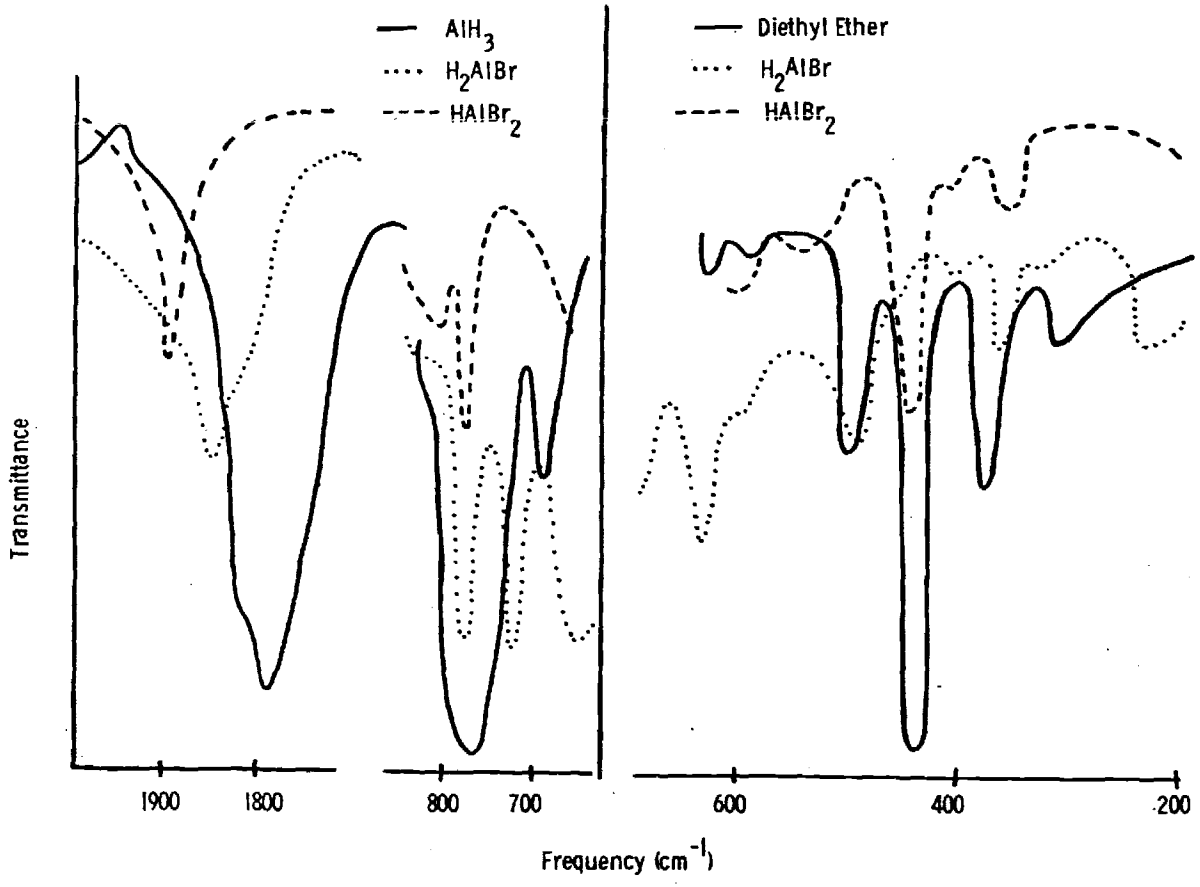

AlH3
H2AlBr
HAlBr2
Diethyl Ether
H2AlBr
HAlBr2
Transmittance
1900
1800
800
700
600
400
200
Frequency (cm-1)

Figure 3. Infrared spectra of (a) the reaction product of $MgBr_2 + AlH_3$ (——) and (b) $MgBr_2 \cdot n(C_2H_5)_2O$ (• • • •).

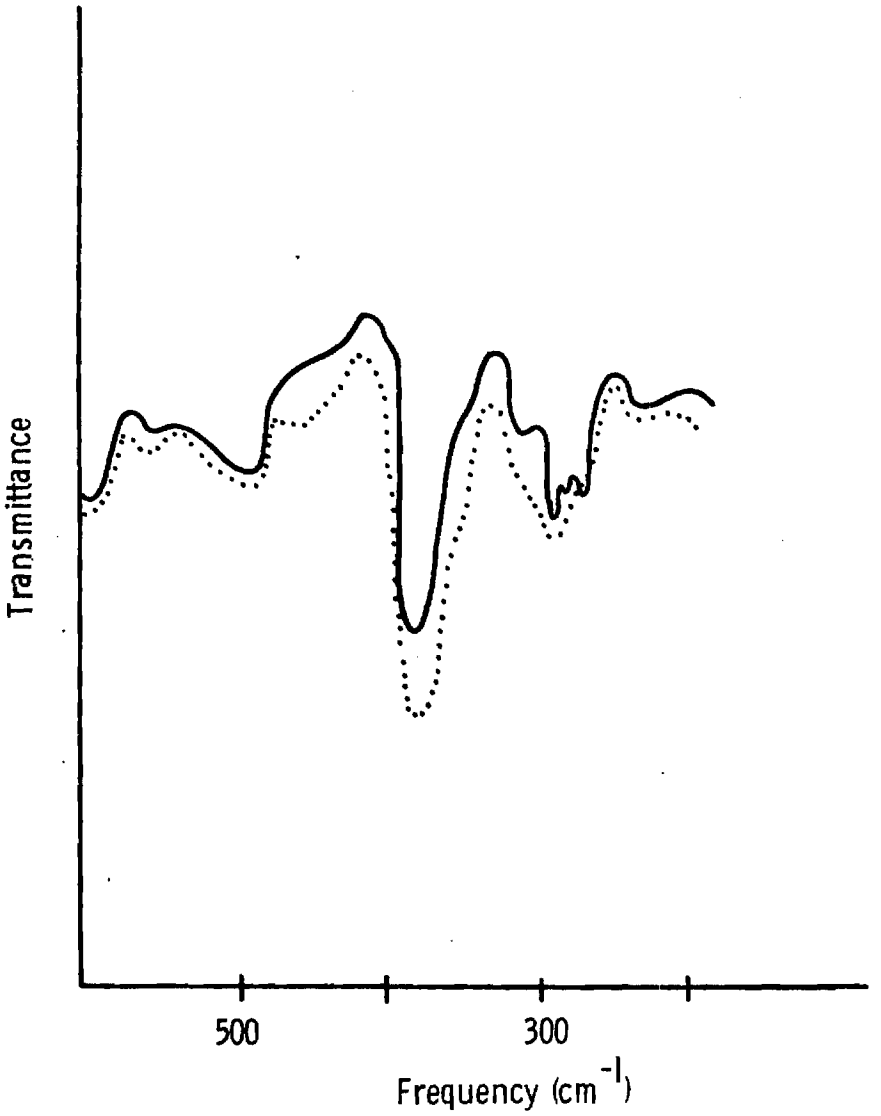

Transmittance
500
300
Frequency (cm^{-1})

Figure 4. Infrared spectra of (a) $ZnCl_2$ (· · · ·)

(b) $ZnCl_2 \cdot 0.11Et_2O$ (- - -) and (c) $H_3Zn_2Cl \cdot 0.35Et_2O$ (——).

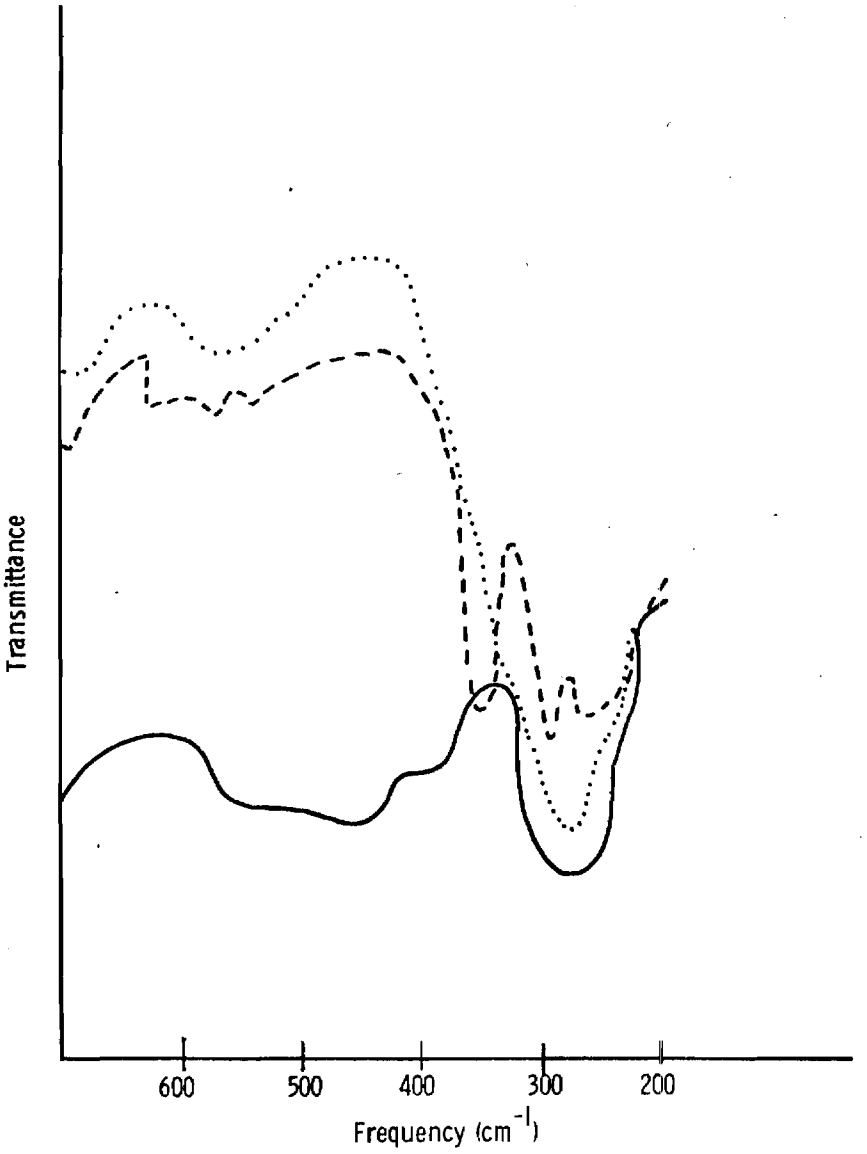
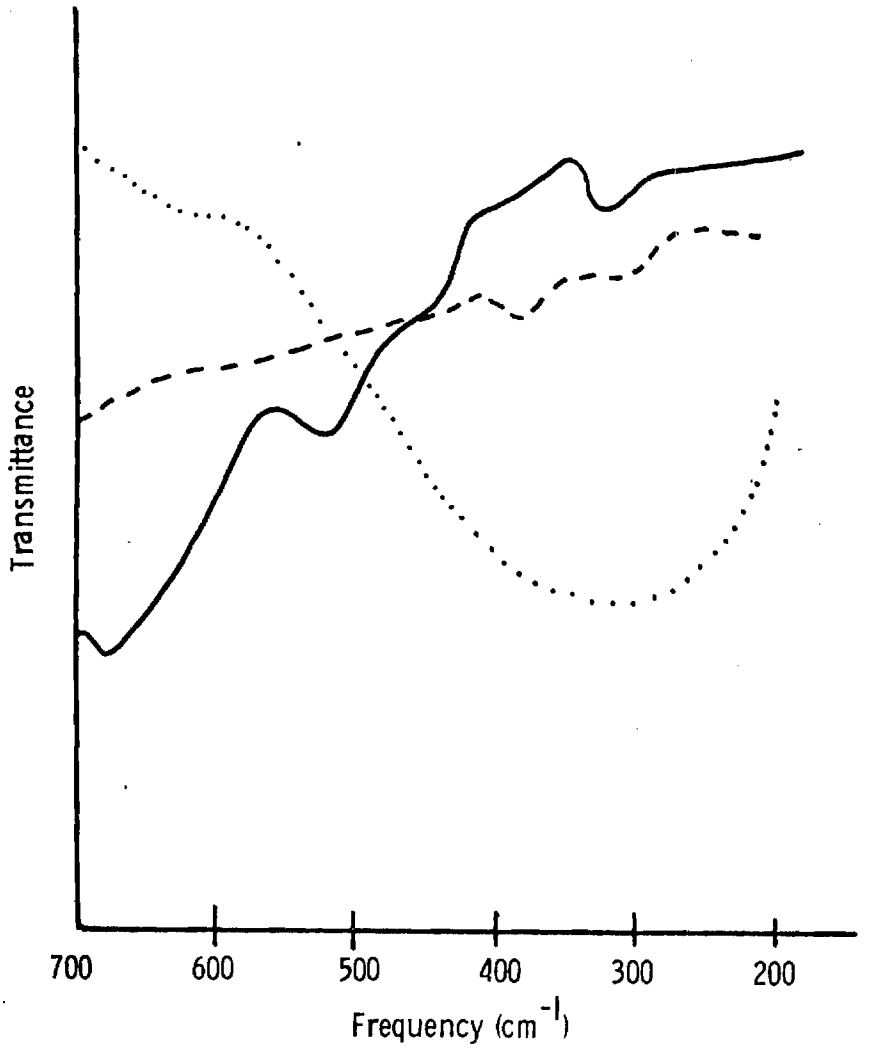

Transmittance
600
500
400
300
200
Frequency (cm^{-1})

Figure 5. Infrared spectra of (a) ZnI_2 (• • •), (b) $ZnI_2 \cdot 0.35Et_2O$ (– –) and (c) $ZnI_2 \cdot AlH_3$ (——).


Transmittance
700
600
500
400
300
200
Frequency (cm^{-1})

Contribution from the Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether

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Received July 13, 1973

The reaction of aluminum hydride with beryllium chloride in diethyl ether has been studied by infrared spectroscopy. The reaction proceeds according to the following equations: $BeCl_2 + AlH_3 \rightarrow H_2AlCl + HBeCl$; $HBeCl + AlH_3 \rightleftharpoons H_2AlCl + BeH_2$. Hydridoberyllium chloride was prepared unequivocally by the reaction of BeH_2 and $BeCl_2$ and shown to be the product of the above reaction. When AlH_3 is used in excess, BeH_2 precipitates from solution. The yield of BeH_2 depends on the amount of excess AlH_3 used. Hydridoberyllium chloride is stable to disproportionation and is dimeric in ether solvent. Difinitive beryllium-hydrogen stretching and deformation frequencies are reported.

Introduction

In a study of the reaction of lithium aluminum hydride with beryllium chloride, we[1] reported experimental results which could be explained by assuming an exchange between aluminum hydride and beryllium chloride to yield hydridoberyllium chloride and dihydridoaluminum chloride (eq 1).

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \quad (1)$$

The suspected HBeCl formed in this reaction was soluble in ether as was the H_2AlCl. However, Dymova[2] has reported that the reaction of lithium aluminum hydride and beryllium chloride in a 2:1 ratio yields $LiAl_2H_7$ and HBeCl which he reports to be insoluble in ether solvent

$$2LiAlH_4 + BeCl_2 \rightarrow HBeCl\downarrow + LiCl\downarrow + LiAl_2H_7 \quad (2)$$

The preparation of $HBeX{\cdot}NR_3$ (X = Cl, Br, I; NR_3 = *N*-methylpyrrolidine and other tertiary amines) by several different methods has been recently reported.[3]

We have undertaken to study the redistribution of AlH_3 with $BeCl_2$ in ether in order to establish (1) the true nature of the products of the reaction of $LiAlH_4$ and $BeCl_2$ in ether, (2) the physical properties of HBeCl, particularly the Be–H stretching and deformation frequencies, and (3) the value of AlH_3 as a reagent for preparing HMX compounds by redistribution of AlH_3 in ether solvent with groups II and III metal halides.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water or on the bench using typical Schlenk-tube techniques.[4]

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 257 infrared spectrophotometer using NaCl liquid cells. Ebullioscopic molecular weight measurements were carried out as described previously.[5]

Reagents. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Benzene (Fisher Certified reagent) was distilled over sodium aluminum hydride immediately prior to use. Anhydrous beryllium chloride was obtained from Columbia Organic Chemical Co. To a slurry of beryllium chloride in benzene cooled to 0° was added excess diethyl ether (50% excess based on the bis(etherate) of beryllium chloride). The resulting solution was then filtered and the benzene was removed from the filtrate under vacuum. The resulting solid was dissolved in ether, and the resulting solution was then standardized by beryllium and chloride analysis. Ether solutions of anhydrous $AlCl_3$ (Fisher Certified reagent) were prepared in a manner similar to that of $BeCl_2$.

Preparation of Aluminum Hydride in Diethyl Ether. Lithium aluminum hydride was added to beryllium chloride in diethyl ether in a 2:1 ratio.[1] The resulting solution was then filtered. Analysis of the filtrate gave an Al:H:Li:Cl ratio of 1.00:3.02:0.06:0.01.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analysis was carried out by titration with EDTA. Chloride was determined by potentiometric titration using Ag-glass electrodes. The sum 3 Al + 2 Be was determined by adding excess NaF to the solution at pH 7.8 and then back-titrating to pH 7.8 using standard hydrochloric acid.

Infrared Study of the Reaction of AlH_3 with $BeCl_2$ in Diethyl Ether. To 15 ml of AlH_3 in ether (0.07 *M*) in a 25-ml volumetric flask was added a volume of $BeCl_2$ in ether (0.225 *M*) calculated to give the desired AlH_3 to $BeCl_2$ ratio. The solution was then adjusted to the 25-ml mark and stirred. AlH_3:$BeCl_2$ ratios of 1:2, 1:1, and 2:1 were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1. They showed no change after 24 hr.

When the $BeCl_2$ was added to the AlH_3 solution, a white precipitate formed immediately. This precipitate redissolved when the AlH_3:$BeCl_2$ ratio was 1:2 or 1:1. In order to identify the precipitate, 30 ml of $BeCl_2$ solution (0.225 *M*) was added to 90 ml of AlH_3 in ether (0.165 *M*). The reaction mixture was then filtered. Analysis of the solid obtained from the filtration gave the following Be:H:Cl ratios: 1.00:1.87:0.25. The amount of beryllium in the solid represented 6.5% of the total beryllium added.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ in Diethyl Ether. The choloroaluminum hydrides, H_2AlCl and $HAlCl_2$, were prepared by mixing AlH_3 and $AlCl_3$ in ether in the appropriate ratios. The reaction between AlH_3 and $AlCl_3$ has been discussed by a number of authors.[6-8] The infrared spectra of AlH_3, H_2AlCl, and $HAlCl_2$ are reported in Figure 2.

Preparation of HBeCl from BeH_2 and $BeCl_2$ in Diethyl Ether. To 6.086 g of $BeBr_2{\cdot}2Et_2O$ in 100 ml of ether was added 35 ml of $LiAlH_4$ in ether (1.119 *M*). The solution was stirred overnight and then filtered. Analysis of the resulting solid gave a Be:H ratio of 1.00:1.90. To 6.80 mmol of this solid product was added 25 ml of $BeCl_2$ in ether (0.2325 *M*). The solution was stirred overnight and filtered. Analysis of the filtrate gave a H:Be:Cl ratio of 0.92:1.00:1.08. The infrared spectrum of the solution *vs.* ether showed bands at 1330, 1050, 970, 908, 840, 840 (sh), 790, and 700 cm^{-1} (see Figure 3).

The compound DBeCl was prepared from BeD_2 and $BeCl_2$ in ether. Its infrared spectrum showed that the band at 1330 cm^{-1} in HBeCl shifted in DBeCl to 985 cm^{-1}. The band at 970 cm^{-1} in HBeCl disappeared in DBeCl. All the other bands in HBeCl were the same in DBeCl. Removal of the ether from the solution of HBeCl yielded an oil which was not characterized further. Ebullioscopic molecular weight determination of HBeCl in ether indicated that this compound is a dimer in the concentration range 0.1–0.3 *m*.

Reaction of AlH_3 with $BeCl_2$ in Et_2O at 4:1 and 8:1 Ratios. To 50 ml of $BeCl_2$ in diethyl ether (0.2067 *M*) was added 17 ml of $LiAlH_4$ in ether (1.156 *M*). The solution was stirred for 1 hr and filtered. To the filtrate which was found to contain no lithium was

(1) E. C. Ashby, J. R. Sanders, P. Claudy, and R. D. Schwartz, *Inorg. Chem.*, 12, 2860 (1973).
(2) T. N. Dymova, M. S. Roshshina, S. Grazullne, and V. A. Kuzneton, *Dokl. Akad. Nauk SSSR*, 184, 1338 (1969).
(3) L. H. Shepherd, G. L. Ter Haar, and F. M. Marlett, *Inorg. Chem.*, 8, 976 (1969).
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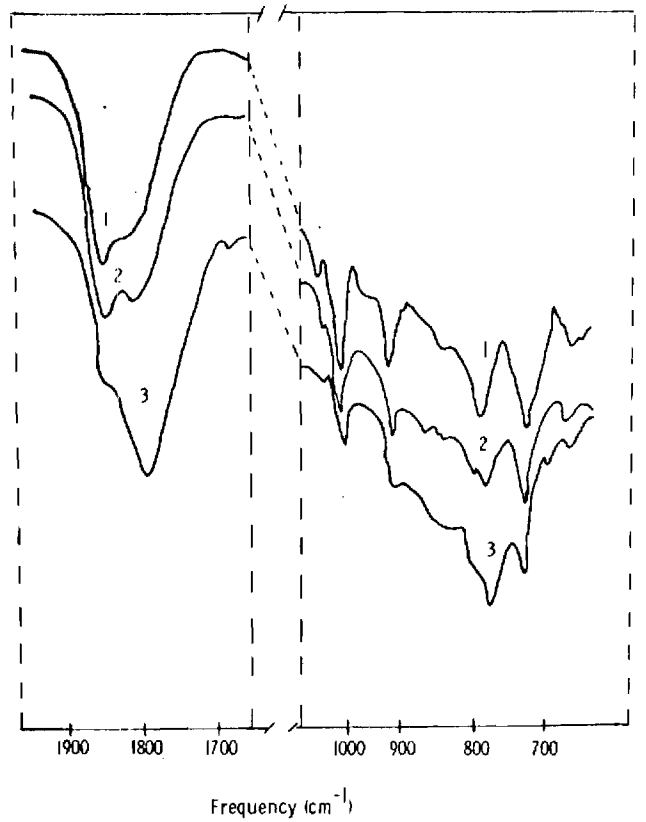


Figure 1. Infrared study of the reaction of AlH_3 with $BeCl_2$ in diethyl ether in (1) 1:2, (2) 1:1, and (3) 2:1 ratios.

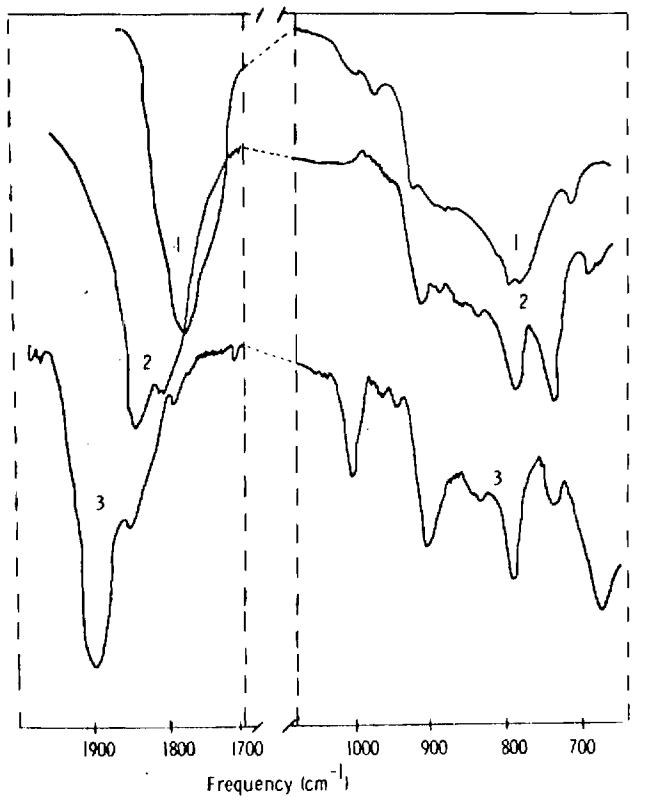


Figure 2. Infrared study of the reactions of AlH_3 with $AlCl_3$ in diethyl ether in (1) 1:0, (2) 2:1, and (3) 1:2 ratios.

added 25 ml of $BeCl_2$ in ether (0.2067 *M*) and the solution was stirred overnight. The solution was then filtered and the resulting solid gave a Be:H ratio of 1.00:1.90. This represented 34.8% of the original amount of beryllium.

In a similar experiment AlH_3 was allowed to react with $BeCl_2$ in ether in a ratio of 8:1. In this case 56% of the original beryllium was isolated in the solid.

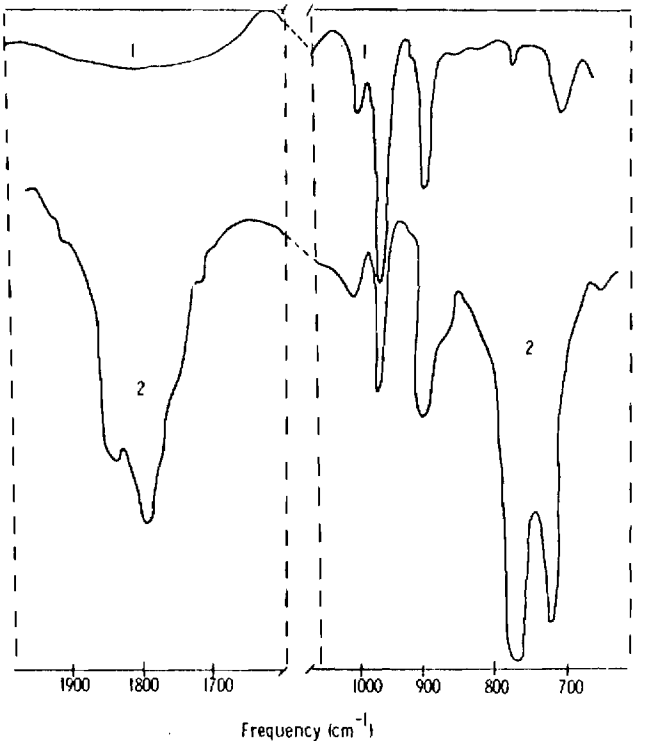


Figure 3. Infrared study of the reaction of (1) BeH_2 with $BeCl_2$ in a 1:1 ratio in diethyl ether and (2) AlH_3 with $BeCl_2$ in a 1:1 ratio in diethyl ether.

Results and Discussion

In our study of the reaction of lithium aluminum hydride with beryllium chloride in diethyl ether in 2:1 ratio, we found that the AlH_3 formed in this reaction is soluble in ether. When the above reaction was carried out in 1:1 ratio, a mixture of products was formed which was attributed to further reaction of AlH_3 with unreacted $BeCl_2$. In an effort to establish the nature of these products we decided to study the reaction of AlH_3 with $BeCl_2$ in ether in some detail.

Since hydrogen-halogen exchange in the AlH_3-$BeCl_2$ system would be expected to form hydridochloroalanes as well as HBeCl, it was decided that the hydridochloroalanes would have to be prepared first for infrared spectroscopic comparison purposes. Ether-soluble alane was found to show bands in its infrared spectrum at 1788 and 770 cm^{-1}. When AlH_3 and $AlCl_3$ were mixed in a ratio of 2:1, H_2AlCl was produced (eq 3). This compound has infrared bands at 1850, 1820 (sh), 780, and 725 cm^{-1}. The compound $HAlCl_2$ was produced when AlH_3 and $AlCl_3$ were allowed to react in 1:2 ratio (eq 4). Its infrared spectrum shows bands

$$2AlH_3 + AlCl_3 \rightarrow 3H_2AlCl \quad (3)$$

$$AlH_3 + 2AlCl_3 \rightarrow 3HAlCl_2 \quad (4)$$

at 1905, 1850, and 780 cm^{-1}.

When $BeCl_2$ was added to AlH_3 in ether in 2:1 ratio, a precipitate formed initially which redissolved as the $BeCl_2$ was added. When the addition was complete, the reaction solution was clear. The infrared spectrum of the solution shows bands at 1850, 970, 905, 780, and 725 cm^{-1}. It is interesting that no bands characteristic of AlH_3 or $HAlCl_2$ are present. The bands at 1850, 780, and 725 cm^{-1} can be attributed to H_2AlCl. The bands at 970 and 905 cm^{-1} were found to correspond to the compound HBeCl prepared independently from BeH_2 and $BeCl_2$. At an AlH_3 to $BeCl_2$ ratio of 1:1, the infrared spectrum of the resulting solution is unchanged. These data indicate that as $BeCl_2$ is added to AlH_3, H_2AlCl and HBeCl are formed

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \quad (5)$$

At an AlH_3:$BeCl_2$ ratio of 2:1, the infrared spectrum showed bands at 1850 (sh), 1788, 970, 905, 772, and 725 cm^{-1}. These data correspond to a mixture of AlH_3 and H_2AlCl. The bands at 970 and 905 cm^{-1} are again attributed to HBeCl. A small amount of solid precipitated from the reaction mixture. The solid was found to be BeH_2 and represented 6% of the total beryllium added. At AlH_3:$BeCl_2$ ratios of 4:1 and 8:1 larger amounts of solid were isolated. This solid proved to be BeH_2 in yields of 34.8 and 56%, respectively. Alane was also found to reduce HBeCl in ether to BeH_2 in 63% yield (based on HBeCl) at an AlH_3:HBeCl ratio of 2:1 (eq 6).

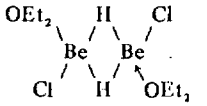
$$2AlH_3 + HBeCl \rightleftharpoons BeH_2\downarrow + H_2AlCl + AlH_3 \quad (6)$$

The compound HBeCl was prepared independently by the redistribution of BeH_2 and $BeCl_2$ in ether (eq 7). The

$$BeH_2 + BeCl_2 \rightarrow 2HBeCl \quad (7)$$

infrared spectrum of HBeCl in ether showed bands at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed that the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl disappeared in DBeCl. This gives a $\nu_H:\nu_D$ ratio of 1.35. Molecular weight determination of HBeCl in ether indicates that the compound is associated with an *i* value of 2.17 at 0.1-0.3 *m*.

Coates and Roberts[9] isolated the complex Be_2H_4·TMED which has a sharp doublet in the infrared spectrum at 1787 and 1807 cm^{-1}. They attribute these bands to terminal Be-H stretching vibrations. We find no bands in this region for HBeCl. Bell and Coates[10] have reported the compounds $[CH_3BeH{\cdot}N(CH_3)_3]_2$ and $[C_2H_5BeH{\cdot}N(CH_3)_3]_2$ which are dimers in benzene. These compounds exhibit strong absorption at 1333-1344 cm^{-1} (in cyclohexane) which is attributed to the Be-H-Be bridge. In the deuterated compounds, the 1344-cm^{-1} band of $[CH_3BeH{\cdot}N(CH_3)_3]_2$ shifted to 1020 cm^{-1}. We therefore conclude that HBeCl is associated through Be-H-Be bridge bonds, *i.e.*



Acknowledgment. We acknowledge with gratitude support of this work by the Office of Naval Research.

Registry No. $BeCl_2$, 7787-47-5; $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; HBeCl, 42016-55-7; $[HBeCl(OEt_2)]_2$, 42744-98-9.

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[Reprinted from Inorganic Chemistry, 13, 2350 (1974).]

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Reaction of Alkali Metal Hydrides with Zinc Halides in Tetrahydrofuran. A Convenient and Economical Preparation of Zinc Hydride

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Received March 14, 1974

AIC40176O

A convenient and economical preparation of ZnH_2 is reported. The reaction of KH with $ZnCl_2$ in 1:2, 1:1, 2:1, and 3:1 molar ratios has been investigated. In these reactions zinc hydride and KCl are initially formed; however, the KCl reacts further with $ZnCl_2$ to form KZn_2Cl_5 and K_2ZnCl_4. The reaction of NaH with $ZnCl_2$ in 1:1 molar ratio forms only ZnH_2 and NaCl. Likewise, the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 in 2:1 molar ratio produced only ZnH_2 and the corresponding alkali metal halide. A more thermally stable form of ZnH_2, which is also more reactive than that prepared by any of the known methods, is produced in these reactions.

Introduction

We have been interested for some time in the preparation of complex metal hydrides where the central metal atom is other than boron or aluminum. Since $NaBH_4$ and $LiAlH_4$ have become such important reagents in synthetic organic chemistry, it would seem important to evaluate complex metal hydrides of other main-group elements for their possible stereoselective properties as reducing agents. In this connection we have reported the preparation of $KMgH_3$,[1] Li_2ZnH_4,[2] $LiCuH_2$,[3] and other complex metal hydrides by the reaction of the corresponding "ate" complex with $LiAlH_4$ (*e.g.*, eq 1 and 2).[2] This synthetic scheme has turned out to be quite good since the complex metal hydride is insoluble in ether and the lithium dimethyldihydridoaluminate is soluble. Thus, the separation of product from by-product is easy and the reaction proceeds in quantitative yield.

$$2CH_3Li + (CH_3)_2Zn \rightarrow Li_2Zn(CH_3)_4 \quad (1)$$

$$Li_2Zn(CH_3)_4 + 2LiAlH_4 \xrightarrow{Et_2O} Li_2ZnH_4\downarrow + 2LiAl(CH_3)_2H_2 \quad (2)$$

It is clear that a more convenient and economical method for the preparation of these compounds would involve the reaction of an alkali metal hydride with the group II metal hydride (*e.g.*, eq 3). This scheme is reasonable since both $NaBH_4$ and $LiAlH_4$ can be prepared in this manner,[4,5] *i.e*

$$3NaH + ZnCl_2 \rightarrow NaZnH_3 + 2NaCl \quad (3)$$

$$4NaH + (CH_3O)_3B \rightarrow NaBH_4 + 3NaOCH_3 \quad (4)$$

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl \quad (5)$$

The purpose of this study, therefore, was to prepare complex metal hydrides of zinc (*e.g.*, $KZnH_3$, K_2ZnH_4, K_3ZnH_5, etc.) by the reaction of an alkali metal hydride with zinc chloride, bromide, or iodide. The hope was that even if such complex metal hydrides could not be prepared by this method, it may be possible to prepare ZnH_2 and/or HZnX compounds and, in addition, elucidate the chemistry of reactions of alkali metal hydrides with zinc halides.

Experimental Section

Apparatus. Reactions were performed under nitrogen using Schlenk tube techniques.[6] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system.[7]

X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually.

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration. Halide was determined by the Volhard procedure.

Materials. Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium at 4000 psig for 24 hr. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared in tetrahydrofuran in the usual manner. Anhydrous zinc chloride, bromide, and iodide were obtained from Fisher Scientific. Tetrahydrofuran (Fisher Certified reagent grade)

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Table I. X-Ray Powder Patterns of Solids from the Reaction of Alkali Metal Hydrides with $ZnCl_2$

Solid from 1:1 reacn of KH with $ZnCl_2$		Solid from 1:2 reacn of KH with $ZnCl_2$		Solid from 2:1 reacn of KH with $ZnCl_2$		Solid from 3:1 reacn of KH with $ZnCl_2$		Solid from 1:1 reacn of KCl with $ZnCl_2$		Solid from reacn of KCl + $ZnCl_2$ filtrate with AlH_3		Solid from 1:1 reacn of NaH with $ZnCl_2$		$ZnCl_2$[a]		KCl[b]		KH[b]		Zn[b]		NaCl[b]	
d, Å	I/I_0[c]	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
5.06	m	6.10	w	3.12	vs	3.28	m	6.10	m	3.12	s	3.22	w	7.6	vs	3.146	s	3.30	vs	2.473	m	3.22	w
3.59	m	5.08	m	2.82	m	3.12	s	5.08	s	2.20	s	2.80	s	6.85	vs	2.224	ms	2.86	s	2.308	m	2.80	s
3.45	vw	4.44	w	2.60	m	2.84	m	4.44	m	1.80	m	2.45	ms	6.31	mw	1.816	m	2.02	s	2.091	s	1.98	s
3.28	vw	3.58	m	2.46	m	2.80	m	3.93	w	1.56	mw	2.31	ms	5.61	w	1.573	w	1.72	s	1.687	m	1.72	w
3.12	s	3.10	vw	2.20	s	2.60	m	3.57	s	1.395	mw	2.08	vs	5.10	vs	1.407	m	1.65	m	1.342	m	1.62	m
2.80	ms	2.89	w	2.08	m	2.46	m	3.40	w	1.273	w	1.98	ms	4.75	vw	1.284	m	1.43	m	1.332	m	1.401	w
2.65	w	2.82	ms	1.90	w	2.20	s	3.10	mw	1.101	vw	1.72	w	4.20	m	1.1126	w	1.31	m	1.237	w	1.256	mw
2.59	ms	2.67	w	1.80	m	2.09	m	2.98	w	1.041	w	1.68	m	4.04	s	1.049	w	1.28	m	1.173	m		
2.44	ms	2.60	ms	1.68	w	2.00	m	2.87	m	0.987	w	1.62	m	3.77	mw	0.9951	w	1.17	m	1.154	w		
2.21	s	2.53	w	1.62	vw	1.90	w	2.67	ms	0.942	w	1.401	w	3.61	s	0.9486	w	1.10	m	1.124	w		
2.01	w	2.46	ms	1.56	mw	1.80	m	2.53	m	0.866	vw	1.333	m	3.31	m	0.9083	vw	1.01	w	1.091	w		
1.90	mw	2.33	w	1.46	m	1.71	m	2.40	w	0.837	vw	1.321	m	3.22	mw	0.8727	w			1.046	w		
1.80	m	2.29	w	1.395	m	1.68	w	2.33	mw			1.256	mw	3.12	s	0.8410	w						
1.71	w	2.25	w	1.360	w	1.64	w	2.25	mw			1.230	w	2.99	w								
1.62	mw	2.08	ms	1.33	w	1.56	mw	2.14	mw			1.169	m	2.95	m								
1.56	mw	1.90	m	1.329	w	1.48	m	2.07	mw			1.148	mw	2.84	w								
1.47	m	1.86	w	1.169	w	1.40	m	1.94	w			1.119	m	2.76	mw								
1.40	m	1.81	vw	1.119	w	1.30	w	1.87	m			1.086	w	2.58	w								
1.378	vw	1.68	w	1.09	w	1.276	m	1.83	mw			1.040	w	2.52	w								
1.280	m	1.62	mw			1.170	w	1.78	w			0.941	w	2.49	w								
1.169	w	1.475	ms			1.109	w	1.70	w					2.45	mw								
1.091	vw	1.370	m			1.043	mw	1.65	w					2.36	s								
1.045	w	1.335	w			0.991	mw	1.57	w					2.25	vw								
1.011	vw	1.329	w					1.54	w					2.18	vw								
0.946	w	1.169	w					1.50	w					2.03	s								
0.939	vw	1.119	w					1.47	w					1.96	w								
0.905	w	1.09	w					1.44	vw					1.88	mw								
0.871	w													1.82	ms								
0.840	w													1.77	ms								
														1.73	ms								

[a] Sample obtained by stripping a THF solution of $ZnCl_2$ to dryness. [b] ASTM file. [c] Key: w, weak; m, medium; s, strong; v, very; d, diffused.

was distilled under nitrogen over $NaAlH_4$. Alane was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration and a lithium-free solution of AlH_3 in THF was obtained.[8]

Potassium, sodium, and lithium hydride were used as a slurry in THF. Each slurry was prepared by washing the respective hydride several times with generous portions of benzene and then several times with THF to remove soluble impurities. The resulting solid, while still under THF, was transferred to a round-bottom flask and more THF was added.

Zinc chloride was fused under vacuum in order to make it anhydrous prior to dissolving in THF. Zinc bromide and iodide were sublimed under vacuum prior to dissolving in THF. The final zinc halide solutions were prepared by stirring the dried zinc halide with THF overnight and filtering the next morning. The zinc iodide solution was stored in the dark.

Reaction of KH with $ZnCl_2$ in THF. (a) Reaction of KH with $ZnCl_2$ in 1:1 Molar Ratio. Potassium hydride slurry (5 mmol) in THF was added to 5 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate revealed that it contained K, Zn, Cl, and H in molar ratios of 1.01:2.00:4.91:0.00. The filtrate contained 1.71 mmol of the starting zinc. An analysis of the solid revealed that it contained K, Zn, Cl, and H in molar ratios of 1.28:1.00:1.71:1.51. The solid contained 3.33 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is given in Table I.

(b) Reaction of KH with $ZnCl_2$ in 1:2 Molar Ratio. Potassium hydride slurry (5 mmol) in THF was added to 10 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 24 hr of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate revealed that it contained K, Zn, Cl, and H in molar ratios of 0.29:1.00:2.27:0.00. The filtrate contained 5.86 mmol of the starting zinc. Analysis of the solid revealed that it contained K, Zn, Cl, and H in molar ratios of 0.82:1.00:1.62:1.19. The solid contained 4.20 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is given in Table I.

(c) Reaction of KH with $ZnCl_2$ in 2:1 Molar Ratio. Potassium hydride slurry (10 mmol) in THF was added to 5 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate showed that it contained none of the starting zinc. Analysis of the solid showed that it contained K, Zn, Cl, and H in molar ratios of 3.08:1.00:1.94:2.97. The solid contained all the starting zinc. Its X-ray powder diffraction pattern is shown in Table I.

Reaction of KCl with $ZnCl_2$ in 1:1 Molar Ratio in THF. A 1.1250-g (15.09-mmol) amount of dry KCl was placed in a 250-ml round-bottom flask and 80 ml of THF was added. $ZnCl_2$ (15.09 mmol) in THF was then added. The mixture was stirred for 4 days, during which time a white solid was always present. The mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate showed that it contained K, Zn, and Cl in molar ratios of 1.06:2.00:4.94. The filtrate contained 10.06 mmol of the starting zinc. Analysis of the solid showed that it contained K, Zn, and Cl in molar ratios of 1.96:1.00:3.94. The solid contained 5.05 mmol of the starting zinc. The X-ray powder pattern of the solid is shown in Table I.

Reaction of AlH_3 with the Filtrate from the Reaction of KCl with $ZnCl_2$ in THF. Alane in THF (20 mmol) was added to the filtrate from the reaction of KCl with $ZnCl_2$ (analysis indicated KZn_2Cl_5). A white precipitate appeared immediately. This slurry was stirred for 1 hr, and then the solid was separated by filtration. The solid was dried under vacuum at room temperature. Analysis of the filtrate showed it to contain K, Zn, Al, Cl, and H in molar ratios of 0.00:0.00:1.00:1.08:2.07. The filtrate contained all of the aluminum. An analysis of the solid showed that it contained K, Zn, Cl, H, and Al in molar ratios of 0.46:1.00:0.52:2.00:0.00. The solid contained all the potassium and zinc. The X-ray powder pattern of the solid is shown in Table I.

Reaction of NaH with $ZnCl_2$ in 1:1 Molar Ratio in THF. Sodium hydride slurry (10 mmol) in THF was added to 10 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 1 day of stirring the mixture was separated by filtration. The solid had turned black while being stirred overnight. The solid was dried under vacuum at room temperature. Analysis of the filtrate showed that it contained Na, Zn, Cl, and H in molar ratios of 0.00:1.00:1.96:0.00. The filtrate contained 5.12 mmol of the starting zinc. Analysis of the solid showed that it contained Na, Zn, Cl, and H in molar ratios of 1.94:1.00:1.97:1.27. The solid contained 4.98 mmol of the starting zinc. The X-ray powder pattern of the solid is shown in Table I.

Reaction of LiH with $ZnBr_2$ in 2:1 Molar Ratio in THF. Lithium hydride slurry (5 mmol) in THF was added to 2.5 mmol of $ZnBr_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate showed it to contain Li, Zn, Br, and H in molar ratios of 1.00:0.02:0.98:0.00. The filtrate contained 0.20 mmol of the starting zinc. Analysis of the solid showed it to contain Li, Zn, Br, and H in molar ratios of 0.03:1.00:0.04:1.89. The solid contained 2.41 mmol of the starting zinc. An X-ray powder diffraction pattern of the solid is shown in Table II.

Reaction of NaH with ZnI_2 in 2:1 Molar Ratio in THF. Sodium hydride slurry (20 mmol) in THF was added to 10 mmol of ZnI_2 in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate showed it to contain Na, Zn, I, and H in molar ratios of 1.06:0.01:1.00:0.00. The filtrate contained 0.21 mmol of the starting zinc. Analysis of the solid showed it to contain Na, Zn, I, and H in molar ratios of 0.06:1.00:0.05:1.97. The solid contained 9.89 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is shown in Table II.

Reaction of NaH with ZnI_2 in 2:1 Molar Ratio in THF in the Presence of $(C_2H_5)_3Al$. A slurry of sodium hydride (15.192 mmol, 30.5 ml) in THF was added to 7.596 mmol (40 ml) of ZnI_2 in THF containing a few drops of $(C_2H_5)_3Al$. The mixture was stirred for a minute and then allowed to settle at room temperature. Analysis of a small portion (1.0 ml) of the clear liquid showed 1.932 mmol of the original zinc in solution. The mixture was stirred further and the

Table II. X-Ray Powder Patterns of Solids from the Reaction of Alkali Metal Hydrides with $ZnBr_2$ and ZnI_2

ZnH_2 from 2:1 reaction of LiH with $ZnBr_2$		ZnH_2 from 2:1 reaction of NaH with ZnI_2		ZnH_2[a] from reaction of $LiAlH_4$ with $(C_2H_5)_2Zn$ in diethyl ether		ZnH_2[b] from reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in diethyl ether	
d, Å	I/I_0[c]	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
4.90	w	4.90	w	4.51	vw	6.27	w
3.79	w	3.79	w	4.23	s	4.50	m
2.82	s	2.82	s	3.80	vw	4.16	m
2.60	s	2.60	s	3.40	m	3.79	m
2.46	s	2.46	s	2.97	vw	3.27	w
2.29	m	2.29	m	2.828	vw	3.12	m
2.08	s	2.08	s	2.608	w	2.94	w
1.90	ms	1.90	ms	2.468	vw	2.83	w
1.68	m	1.68	m	2.387	m	2.61	vw
1.62	ms	1.62	ms	2.290	m	2.50	w
1.475	s	1.475	s	2.225	m	2.40	w
1.370	ms	1.370	ms	2.135	w	2.29	w
1.335	m	1.335	m	2.085	w	2.23	m
1.329	m	1.329	m	2.107	vw	2.18	m
1.300	w	1.300	w	1.905	w	2.14	vvw
1.234	w	1.234	w	1.764	w	2.08	m
1.169	m	1.169	m	1.688	vw	2.02	vw
1.150	w	1.150	w	1.630	vw	1.98	vw
1.119	m	1.119	m	1.562	vw	1.90	vw
1.09	m	1.09	m	1.486	vw	1.77	w
1.04	mw	1.04	mw	1.464	vw	1.63	vvw
1.013	mw	1.013	mw	1.416	vw	1.61	vvw
0.974	mw	0.974	mw	1.336	vw	1.57	vvw
				1.305	vw	1.51	w
				1.295	vw	1.42	vw
				1.259	vw	1.35	w
				1.219	vw		
				1.172	vw		
				1.157	vw		
				1.123	vw		

[a] See ref 5. [b] See ref 8. [c] Key: w, weak; m, medium; s, strong; v, very; d, diffused.

(8) H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, 88, 1464 (1966).

clear supernatent liquid was analyzed for zinc at 30 min, 1 hr, 2 hr, and 5 hr intervals. After 5 hr the analysis of clear liquid showed only 0.94 mmol of the original zinc and it was noticed that the color of the reaction mixture gradually turned black. The reaction mixture was stirred for 20 hr and then filtered. Analysis of the filtrate showed it to contain Na, Zn, I, and H in molar ratios of 1.02:0.02:1.00:0.00 and the filtrate contained 0.30 mmol of the original zinc. Analysis of the black residue showed it to contain only zinc.

Results and Discussion

The reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 in 2:1 molar ratio in THF proceeds according to eq 6 and 7. In

$$2LiH + ZnBr_2 \rightarrow 2LiBr + ZnH_2 \quad (6)$$

$$2NaH + ZnI_2 \rightarrow 2NaI + ZnH_2 \quad (7)$$

both cases the alkali metal halide remains in solution while the ZnH_2 precipitates. In both cases all of the alkali metal and halide are found in solution, while all of the zinc and active hydride precipitate from solution. The X-ray powder patterns of the ZnH_2 obtained from these two reactions are shown in Table II. Also given in Table II are the X-ray powder patterns of ZnH_2 prepared by the reaction of $LiAlH_4$ with $(C_2H_5)_2Zn$[9] and $(CH_3)_2Zn$.[10] The latter two patterns differ from one another, as well as from the pattern of ZnH_2 prepared in this study. However, the X-ray powder patterns of ZnH_2 prepared by the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 are identical. It has been our experience that ZnH_2 prepared by the reaction of $LiAlH_4$ with a dialkylzinc compound is usually amorphous, yielding an X-ray powder pattern with only two broad, diffuse lines, one at a *d* spacing of about 4.0 and the other at 2.5. Indeed, two reports in the recent literature[9,10] claim different X-ray powder patterns for ZnH_2 prepared by the latter method. In addition, ZnH_2 prepared by the Schlesinger method ($LiAlH_4 + R_2Zn$) turns black after a few days at room temperature and hydrolyzes slowly with water. The ZnH_2 prepared in the present study remains white for several weeks and hydrolyzes rapidly with water at room temperature, in addition to giving a distinct, reproducible powder pattern. However, it does decompose thermally at 90° to produce zinc metal and hydrogen.

The reactions of KH with $ZnCl_2$ in 1:2, 1:1, 2:1, and 3:1 molar ratios proceed according to eq 8–11. In the reaction

$$KH + 2ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_2ZnCl_2 + {}^1/_3K_2ZnCl_4\downarrow + {}^1/_2ZnH_2\downarrow \quad (8)$$

$$2KH + ZnCl_2 \rightarrow {}^1/_6KZn_2Cl_5 + {}^1/_6K_2ZnCl_4\downarrow + {}^1/_2KCl\downarrow + {}^1/_2ZnH_2\downarrow \quad (9)$$

$$2KH + ZnCl_2 \rightarrow 2KCl\downarrow + ZnH_2\downarrow \quad (10)$$

$$3KH + ZnCl_2 \rightarrow KH\downarrow + 2KCl\downarrow + ZnH_2\downarrow \quad (11)$$

of KH with $ZnCl_2$ in a 1:2 molar ratio, KZn_2Cl_5 remains in solution, while K_2ZnCl_4 and ZnH_2 precipitate from solution. This statement is supported by the fact that the filtrate from this reaction mixture contained K, Zn, Cl, and H in molar ratios of 0.29:1.00:2.27:0.00 and 58.6% of the starting zinc. A mixture of ${}^1/_3KZn_2Cl_5 + {}^1/_2ZnCl_2$ will have K, Zn, and Cl in molar ratios of 0.282:1.00:2.28 and will contain $(({}^3/_2 + {}^1/_2)/2)100 + 58.5\%$ of the starting zinc. The solid from the reaction mixture contained K, Zn, Cl, and H in molar ratios of 0.82:1.00:1.62:1.19. A mixture of ${}^1/_3K_2ZnCl_4 + {}^1/_2ZnH_2$ will have K, Zn, Cl, and H in molar ratios of 0.80:1.00:1.60:1.21. The X-ray powder diffraction pattern of the solid (shown in Table I) corresponds to a mixture of K_2ZnCl_4 and ZnH_2. The pattern for ZnH_2 in the mixture is the same as that for ZnH_2 produced by the reactions of LiH with $ZnBr_2$ and NaH with ZnI_2.

At this stage it might be interesting to consider the origin of the KZn_2Cl_5 found in the filtrate and the K_2ZnCl_4 found in the precipitate. The reaction between KCl and $ZnCl_2$ in a 1:1 molar ratio is shown in eq 12. The filtrate from this

$$KCl + ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_3K_2ZnCl_4 \quad (12)$$

reaction mixture contains K, Zn, and Cl in molar ratios of 0.06:2.00:4.94 and two-thirds of the starting zinc. The solid contains K, Zn, and Cl in molar ratios of 1.96:1.00:3.94 and one-third of the starting zinc. The analytical data are consistent with the proposed reaction products. The solid product is not a physical mixture of KCl and $ZnCl_2$ in 2:1 ratio since the X-ray powder diffraction pattern (shown in Table I) of the product contains no lines common to either KCl or $ZnCl_2$. Thus, the solid product is presumed to be a true coordination compound (K_2ZnCl_4). The compound in the filtrate is represented as KZn_2Cl_5 for two reasons. First, KCl is not soluble in THF; therefore if it is in solution, it should be present as a complex. Second, if the remaining KCl is not complexed to $ZnCl_2$ as KZn_2Cl_5, one would expect to see all of the KCl react with half of the $ZnCl_2$ to give ${}^1/_2$ equiv of K_2ZnCl_4, instead of ${}^1/_3$ equiv. In the latter case, one would expect to find half the starting zinc in the filtrate and half in the solid. This is not what is observed and therefore KZn_2Cl_5 must be a true coordination complex.[11]

An opportunity was given for KZn_2Cl_5 to react with AlH_3 to form KZn_2H_5. The reaction of KZn_2Cl_5 with AlH_3 yielded a white solid containing K, Zn, Cl, H in molar ratios of 0.46:1.00:0.52:2.00. The X-ray powder pattern of the solid (shown in Table I) contains lines for KCl, and therefore it must be a mixture of KCl and ZnH_2. The ZnH_2 formed in this reaction did not show any distinct lines; therefore, it must be amorphous, as is the ZnH_2 that sometimes is produced from the reaction of $LiAlH_4$ with a dialkylzinc compound. The complex KZn_2Cl_5 evidently is not completely reduced to KZn_2H_5, but instead KCl and ZnH_2 are formed.

With this information, one can write a reasonable sequence (eq 13 and 14) for the reaction of KH with $ZnCl_2$ in 1:2

$$KH + 2ZnCl_2 \rightarrow KCl + {}^1/_2ZnH_2 + {}^3/_2ZnCl_2 \quad (13)$$

$$KCl + ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_3K_2ZnCl_4 \quad (14)$$

molar ratio. First, KH reacts with 2 equiv of $ZnCl_2$ to give 1 equiv of KCl, ${}^1/_2$ equiv of ZnH_2, and ${}^3/_2$ equiv of $ZnCl_2$. After this, the KCl reacts with 1 equiv of $ZnCl_2$ to give ${}^1/_3$ equiv each of KZn_2Cl_5 and K_2ZnCl_4.

The reactions of KH with $ZnCl_2$ in 1:1, 2:1, and 3:1 molar ratios are similar to the reaction just discussed. The first step is the maximum conversion of KH into KCl with the simultaneous formation of ZnH_2. Then, if any $ZnCl_2$ remains, KCl reacts with it to give KZn_2Cl_5 and K_2ZnCl_4. The total reactions as written in eq 9–11 are supported by analytical and X-ray powder diffraction data (Table I). It

(9) E. C. Ashby and R. G. Beach, *Inorg. Chem.*, 10, 2486 (1971).

(10) D. J. Shriver, G. J. Kubas, and J. A. Marshall, *J. Amer. Chem. Soc.*, 93, 5067 (1971).

(11) One of the reviewers suggested that K_2ZnCl_4 and KZn_2Cl_5 might be cocrystallates of KCl and $ZnCl_2$. In order to be able to establish the authenticity of $Zn_2Cl_5^-$ and $ZnCl_4^-$ anions, one would need the corresponding interatomic distances to support such a claim. These interatomic distances are not available at the present time. However, X-ray powder diffraction patterns are available and these powder patterns do show that the above compounds are not simple physical mixtures of KCl and $ZnCl_2$. Thus, if these compound are cocrystallates of KCl and $ZnCl_2$, it does seem more than just fortuitous that the analytical data would turn out as it did. For KZn_2Cl_5, the molar ratios of K, Zn, and Cl were 1.06:2.00:4.94. For K_2ZnCl_4, the molar ratios of K, Zn, Cl were 1.96:1.00:3.94.

is important to note that the ZnH_2 formed in all these reactions of KH with $ZnCl_2$ gives the same powder pattern as the ZnH_2 prepared by the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2.

The reaction of NaH with $ZnCl_2$ in 1:1 molar ratio proceeds according to eq 15. The filtrate from this reaction

$$NaH + ZnCl_2 \rightarrow {}^1/_2ZnCl_2 + NaCl + {}^1/_2ZnH_2 \quad (15)$$

contained Na, Zn, Cl, and H in molar ratios of 0.00:1.00:1.96:0.00 and half the starting zinc. The solid contained Na, Zn, Cl, and H in molar ratios of 1.94:1.00:1.97:1.27. The analytical data support the reaction as written and the X-ray powder pattern of the solid (Table I) contained lines only for NaCl and zinc metal. The powder pattern for ZnH_2 seen in the other cases was not observed. Also, this was the only reaction between an alkali metal hydride and zinc halide where the ZnH_2 produced turned black after just a few days. Why the ZnH_2 from this reaction behaved thus is unknown at present.

Several salient points about ZnH_2 are worth noting at this point. First, ZnH_2 is an isolable species which has moderate stability at or below room temperature. Second, ZnH_2 is the most thermally stable of the group IIb hydrides. Cadmium hydride[12,13] and mercury hydride[12] decompose rapidly even below 0°. Third, ZnH_2 exhibits ready reactivity in situations where the product is soluble.[12,14] The ZnH_2 prepared in this study remains stable longer and is more reactive than ZnH_2 prepared by the Schlesinger method. In view of point 3 we are presently studying ZnH_2 as a reducing agent toward organic substrates.[15]

Acknowledgment. We are indebted to the Office of Naval Research, under Contract No. N-14-67-A-0159-005, for support of this research.

Registry No. KH, 7693-26-7; KCl, 7447-40-7; AlH_3, 7784-21-6; NaH, 7646-69-7; LiH, 7580-67-8; ZnH_2, 14018-82-7; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; KZn_2Cl_5, 52002-83-2.

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(15) Note Added in Proof. The reaction of NaH with ZnI_2 in 2:1 molar ratio in THF produces ZnH_2 in essentially quantitative yield when the reaction mixture is allowed to stir for 24–48 hr. It has been suggested that the reaction time might be reduced by using triethylaluminum as a catalyst to solubilize the NaH as $NaAl(C_2H_5)_3H$. This idea was tested by repeating the above reaction in the presence of a catalytic amount of triethylaluminum. The reaction time was reduced considerably in the initial stages of the reaction; however, at least 24 hr was required for complete reaction and the final product turned black during the reaction period unlike the uncatalyzed reaction.

Preparation of the First Stable Complex Metal Hydride of Copper, $LiCuH_2$

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Summary Reaction of $LiCuMe_2$ at low temperature with $LiAlH_4$ in diethyl ether results in the formation of a highly pyrophoric solid whose analysis is consistent with the formula $LiCuH_2$, and which is stable as an etherate.

Recently, there has been considerable interest in copper chemistry, in particular in synthetic applications involving lithium alkylcuprates[1] and copper hydride.[2,3] In view of the unusual chemistry of these reagents, we have been interested in the preparation of stable complex metal hydrides of copper in order to study their usefulness as reducing agents in organic chemistry.

Copper hydride prepared in ether is not stable at room temperature, decomposing with evolution of hydrogen to form a black solid.[4] Stable solutions of CuH in pyridine have been prepared by Dilts and Shriver[2] who have shown that the solubility of CuH is due to its complexation with the Lewis base. Stable complexes of CuH with PPh_3 have also been prepared by Churchill and his co-workers.[3] An *X*-Ray crystal structure determination showed CuH to be hexameric. This ability of CuH to undergo complex formation suggested to us that it should be possible to synthesize complex metal hydrides of copper. Monnier has claimed the preparation of $CuAlH_4$ at $-80°$ by the reaction of Li_2CuBr_4 with $LiAlH_4$. However, the $CuAlH_4$ formed was not stable above $-80°$ and decomposed to Cu, CuH, Al, and H_2.[5] Our experience with complex metal hydrides of zinc (*e.g.*, $LiZnH_3$, Li_2ZnH_4, *etc.*) suggest that complex metal hydrides of copper should be more stable than CuH itself.[6]

We have prepared a complex metal hydride of copper, which is more stable than CuH, by the reaction of lithium dimethylcuprate with $LiAlH_4$ in Et_2O (Scheme). To a slurry of CuI (18 mmol) in Et_2O (200 ml) at $-78°$ was added MeLi (36 mmol) in ether. The mixture was stirred for 1 h at $-78°$, at which time all the CuI had dissolved. $LiAlH_4$ (18 mmol) in ether was then added. No precitate formed at $-78°$; however, while warming the solution to room temperature, a yellow precipitate formed. The mixture was filtered and the yellow solid isolated as an ether slurry. This slurry gave the following analysis. Li; Cu; H; Al; 1·03; 1·0; 2·06; 0·08. The i.r. spectrum of the filtrate corresponded to that of an authentic sample of $LiAlH_2Me_2$ prepared by the redistribution of $LiAlMe_4$ and $LiAlH_4$. The yellow solid was filtered off and dried *in vacuo*.† Differential thermal analysis–thermogravimetric analysis of the solid $LiCuH_2$ etherate shows violent decomposition at 70° with the evolution of ether. No sharp lines, but two broad diffuse lines were observed in the *X*-ray powder pattern of the solid $LiCuH_2$. When stored as an ether slurry, $LiCuH_2$ is stable at room temperature for several days, unlike CuH alone (prepared in diethyl ether) which decomposes immediately on warming to room temperature.[4] We have studied the preparation of this compound and other stoicheiometric complex metal hydrides of copper, *e.g.*, Li_3CuH_4, under a variety of conditions and in different solvents, and we shall report on this study elsewhere.

Reduction of model α,β-unsaturated ketones by $LiCuH_2$ is in progress.

$$MeLi + CuI \longrightarrow MeCu + LiI$$

$$MeCu + MeLi \longrightarrow LiCuMe_2$$

$$LiCuMe_2 + LiAlH_4 \longrightarrow LiCuH_2 + LiAlMe_2H_2$$

Scheme

† Prolonged subjection of the yellow solid ($LiCuH_2$) to reduced pressure in order to remove the ether of solvation resulted in decomposition. The dry yellow solid was stable at room temperature for at least several days; however, owing to its great sensitivity to O_2 and H_2O, it was generally stored as an ether slurry prior to use.

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(*Received*, 18*th September* 1973; *Com.* 1298.)

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Georgia Institute of Technology	Non-classified
	2b. GROUP

3. REPORT TITLE

Complex Metal Hydrides

High Energy Fuel Components for Solid Propellant Rocket Motors

4. DESCRIPTIVE NOTES (*Type of report and, inclusive dates*)

5. AUTHOR(S) (*First name, middle initial, last name*)

Eugene C. Ashby

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
	180	122

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. N00014-67-A-0159-005	
c. NA	9b. OTHER REPORT NO(S) (*Any other numbers that may be assigned this report*)
d.	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

During the past contract period work has continued on the preparation and structure elucidation of simple and complex metal hydrides of the main group elements. The new hydrides $Mg(ZnH_3)_2$ and $MgZnH_4$ are reported for the first time as well as new and simple routes for the preparation of complex metal hydrides of beryllium; e.g. Li_2BeH_4 and Li_3BeH_5. Since the last period, four manuscripts were written for publication which are now "in press" and three additional manuscripts have appeared in the literature.

DD FORM 1 NOV 65 1473 (PAGE 1)

/N 0101-807-6811

Security Classification

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Complex Metal Hydrides						
High Energy Fuels						
Organometallic Compounds						
High Energy Binders						
Burning Rate Accelerators						
Solid Rocket Propellant						

DD FORM 1 NOV 65 1473 (BACK)

S/N 0101-807-6821

Security Classification

A-31403